

JOURNAL OF THE CHEMICAL SOCIETY.

ABSTRACTS OF PAPERS ON ORGANIC CHEMISTRY.

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ABSTRACTS OF CHEMICAL PAPERS PUBLISHED IN
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PART I.

Organic Chemistry.

Purification of Acetylene. By FRITZ ULLMANN and IRMA GOLDBERG (*Chem. Centr.*, 1899, ii, 19—20; from *J. Gasbel.*, 42, 374—377).—The phosphorus and sulphur in samples of acetylene which had been purified by various methods were estimated by Lunge and Cedercreutz's method (*Abstr.*, 1898, ii, 54). The results showed that ferric and chromic salts have no purifying effect on crude acetylene, and that whilst cuprous chloride removes hydrogen phosphide but not organic sulphur compounds, chromic acid absorbs, not only the phosphorus compounds, but also almost all those containing sulphur.

The chromic acid contained in the solution used for purifying acetylene is estimated as follows. 25 grams are boiled with 100 c.c. of a 5 per cent. sodium hydroxide solution, the cooled liquid made up to a litre, and 50 c.c. then treated with 8 c.c. of a 10 per cent. solution of potassium iodide, together with about 18 c.c. of a 20 per cent. solution of hydrochloric acid, 200 c.c. of water, and a slight excess of sodium thiosulphate solution. The excess of thiosulphate is titrated with iodine solution. The results obtained show that pure acetylene is not attacked by the chromic acid solution and that the amount of solution required for purifying the gas is dependent on the quantity of gas to be treated and amount of impurity it contains.

E. W. W.

The Heating of, and Evolution of Chlorine from, Bleaching Powder Purifiers for Acetylene. By FELIX B. AHRENS (*Zeit. angew. Chem.*, 1899, 777—779).—When a mixture of bleaching powder and sawdust is employed to remove the sulphur and phos

phorus compounds present as impurities in commercial acetylene, it is found that the gas, after passing through the purifiers, contains a large amount of some chlorine compound, and, moreover, after a short time, the mixture becomes strongly heated and loses its purifying properties. This result is not due to the action of acetylene on the mixture, because when bleaching powder, sawdust, and water are intimately mixed, a considerable rise of temperature occurs more or less rapidly and large quantities of chlorine and water vapour are evolved. The relationship between the composition of the mixture and the time required to reach the maximum temperature is given in a table. A similar result is obtained when sawdust is added to a cold solution of calcium hypochlorite; after a short interval, the temperature rises to 95° . No alteration of temperature is noted when pure, finely divided cellulose is substituted for sawdust. These experiments indicate that it is the lignin of the latter substance which reacts with the hypochlorite. The disadvantages attendant on the employment of sawdust may be entirely obviated by mixing the bleaching powder with some inert material, such as infusorial earth, powdered coke, brick-dust, or lead chromate. G. T. M.

Tri- and Tetra-halogen-substituted Methanes. By JOHN ULRIC NEF (*Annalen*, 1899, 308, 329—333. Compare Abstr., 1898, i, 102).—Alcoholic potash (1 mol.), sodium ethoxide, or potassium cyanide converts carbon tetrabromide into bromoform, but no alkali carbonate is produced; excess of alcoholic potash (6 mols.) yields carbon monoxide and ethylene, but again without production of carbonate. Carbon tetraiodide behaves in the same way, but carbon tetrachloride yields carbon monoxide and ethylic orthoformate. The behaviour of these compounds is therefore analogous to that of iodophenylacetylene; the halogen appears to assume the tervalent condition, and the resulting compound, $CX_3 \cdot XH \cdot OEt$, dissociates into CHX_3 , $CHMe \cdot CHO$, and HX . Chloropicrin yields ethyl orthocarbonate when treated with sodium ethoxide, and ammonia converts it into guanidine; contrary to the statement of Bolas and Groves (this Journal, 1870, 23, 164; 1871, 24, 783), triphenylguanidine is not produced when aniline acts on carbon tetrabromide.

Carbon tetrabromide and finely divided silver at 120 — 180° yield only silver bromide and carbon; bromoform under the same conditions yields no gas, but at 200° pure acetylene is evolved. Iodoform and finely divided silver at 100° in an atmosphere of carbon dioxide become ignited, and yield carbon, iodine, methane, and acetylene. When bromoform vapour is passed over strongly heated copper in an atmosphere of carbon dioxide under reduced pressure, methane is produced, and the same result attends the reduction of bromoform with zinc dust and alcohol.

Iodoform and acetone at 135 — 150° yield the compound, $C_8H_{11}I$, which boils at 74° under 35 mm. pressure; an equal proportion of methylene iodide is also formed. M. O. F.

Solid Butadiene Dibromide. By JOHANNES THIELE (*Annalen*, 1899, 308, 333—343. Compare Abstr., 1899, i, 554).—According to the author's theory of unsaturated compounds (*loc. cit.*), butadiene,

$\text{CH}_2\cdot\text{CH}\cdot\text{CH}\cdot\text{CH}_2$, should yield an $\alpha\delta$ -dibromide on direct addition of bromine; this is now found to be the case, as the initial product is the solid dibromide melting at 53° (compare Griner, *Abstr.*, 1893, i, 450). The constitution of the solid dibromide is established by oxidation, which converts it into $\alpha\delta$ -dibromo- $\beta\gamma$ -dihydroxybutane; further oxidation gives rise to bromacetic acid, unaccompanied by $\alpha\beta$ -dibromopropionic acid. M. O. F.

Nitrosates. By WLADIMIR IPATIEFF (*Chem. Centr.*, 1899, ii, 178; from *J. Russ. Chem. Soc.*, 1899, 31, 441—452).—The *nitrosate* from δ -methyl- Δ^7 -amylene, $\text{NO}_2\cdot\text{O}\cdot\text{CMe}_2\cdot\text{C}(\text{NOH})\cdot\text{CH}_2\text{Me}$, prepared by Wallach's method, crystallises from benzene, melts and decomposes at 105° , and after boiling with hydrochloric acid, reduces Fehling's solution; by the action of aniline dissolved in alcohol, it is converted into a crystalline compound. The *nitrosate* from γ -ethyl- Δ^8 -amylene, $\text{NO}_2\cdot\text{O}\cdot\text{CEt}_2\cdot\text{CMe}\cdot\text{NOH}$, crystallises from hot benzene in prisms, melts and decomposes at 80 — 81° and by the action of an alcoholic solution of aniline forms the *nitrolanilide*, $\text{NOH}\cdot\text{C}_7\text{H}_{13}\cdot\text{NPh}$; the latter crystallises in colourless prisms, melts at 123 — 124° , and is easily soluble in chloroform, ether, or hot alcohol. By the action of potassium nitrite on an acid solution of the hydrochloride, the crystalline compound, $\text{NOH}\cdot\text{C}_7\text{H}_{13}\cdot\text{NPh}\cdot\text{NO}$, is obtained, and by warming the hydrochloride with hydrochloric acid, a ketoanilide is formed. The *nitrosate* from γ -methyl- Δ^8 -amylene, $\text{NO}_2\cdot\text{O}\cdot\text{CMeEt}\cdot\text{CMe}\cdot\text{NOH}$, crystallises from benzene and melts and decomposes at 85° . The corresponding *nitrolanilide*, $\text{NOH}\cdot\text{C}_5\text{H}_{11}\cdot\text{NPh}$, crystallises from ether or hot alcohol in large, colourless, easily soluble prisms and melts at 78 — 79° . The *hydrochloride*, $\text{C}_{12}\text{H}_{18}\text{ON}_2\cdot\text{HCl}$, yields a nitroso-compound by the action of potassium nitrite, and when boiled with hydrochloric acid forms a ketoanilide. Δ^8 -Hexylene containing the group $\cdot\text{CH}\cdot\text{CH}\cdot$ yields an oily nitrosate of sp. gr. greater than 1.

[With A. SOLONINA.]—The nitrosates of Δ^8 -amylene and γ -methyl- Δ^8 -butylene are oils, and diamylene does not form a crystalline nitrosate. Ethyl dimethylallylmalonate which contains the group $\cdot\text{C}\cdot\text{CH}$, forms a nitrosate which melts at 104 — 105° and after boiling with hydrochloric acid reduces Fehling's solution.

Crystalline nitrosates are obtained from compounds which contain the group $\cdot\text{C}\cdot\text{CH}$, and probably also from those containing the group $\cdot\text{C}\cdot\text{C}\cdot$ (Demjanoff, *J. Russ. Chem. Soc.*, 1896, 28, 895). E. W. W.

Hydrogenation of Allyl Alcohol. By N. SPERANSKI (*Chem. Centr.*, 1899, ii, 181; from *J. Russ. Chem. Soc.*, 1899, 31, 423—426).—By adding aluminium shavings to a mixture of allyl alcohol with a 25 per cent. solution of potassium hydroxide and cooling the product for five days, the odour of allyl alcohol disappears and a 15 per cent. yield of normal propyl alcohol is obtained. E. W. W.

Simultaneous Oxidation and Hydration of Organic Compounds under the Influence of Light and Oxygen. By MARCELLIN P. E. BERTHELOT (*Compt. rend.*, 1899, 129, 627—636. Compare Richardson and Fortey, *Trans.*, 1896, 1352).—A study of chemical reactions under conditions which render them comparable with the

changes which take place in animal and vegetable organisms. Pure ether in the presence of air and water, or of air and a solution of hydrogen peroxide, suffers no change when kept in the dark. If, however, it is exposed to direct sunlight for five months, the hydrogen peroxide is completely decomposed, and the whole of the liberated oxygen as well as that of the air is absorbed, and methane, acetic acid, acetaldehyde, and ethyl alcohol are produced.

Tubes completely filled with ether, or ether and water, were exposed to sunlight for $1\frac{1}{2}$ months; on examination, the ether was found to have suffered no change.

In 1882, several flasks were completely filled with ether and then hermetically sealed; these were opened in August, 1899, when the ether was found to be quite unchanged. A stoppered bottle which in 1882 contained pure ether, was in 1899 found to contain less than half the weight of a liquid which was free from ether, and consisted of ethyl acetate, ethyl alcohol, acetic acid, and water.

H. R. LE S.

Dissociation of Alkyl Salts of Nitric Acid, Sulphuric Acid, and the Halogen Hydrides. By JOHN ULRIC NEF (*Annalen*, 1899, 309, 126—189. Compare Abstr., 1898, i, 102).—As a preliminary to studying the progress of dissociation in the sugar group, the author has made a number of experiments on the behaviour of alkyl haloids towards alcoholic potash and sodium ethoxide, various salts of silver in presence of alcohol, amines, and ethyl sodiomalonate, and on the dissociation of alkyl nitrates and alkyl sulphates.

The author recognises two classes of dissociation of alkyl haloids, by which these compounds are resolved into halogen hydride, on the one hand, and either (I) a substituted methylene, such as ethylidene, or (II) an olefine, on the other. From an investigation of the behaviour of alkyl haloids towards alcoholic potash, the conclusion is drawn that, in this case, both forms of dissociation proceed simultaneously, the production of ethers depending exclusively on addition of alcohol to alkylidene. The nature of the radicles in various primary alkyl iodides, $\text{CHRR}'\cdot\text{CH}_2\text{I}$, exerts a remarkable influence on the proportion of one form of dissociation to the other; alkyl chlorides undergo more alkylidene dissociation than the corresponding bromides, whilst the iodides yield more olefine than the bromides. The same products are obtained when either alcoholic potash or sodium methoxide is employed, but the latter acts more slowly.

It is impossible to deal adequately with this paper in an abstract, because it is composed of the descriptions of numerous experiments with well known substances, interspersed with theoretical considerations suggested by the results.

Tertiary butyl isocyanide, which, according to the author's views on bivalent carbon, has the formula $\text{CMe}_3\cdot\text{N}:\text{C}$, is prepared from tertiary butyl iodide and silver cyanide, and boils at 91° ; it has a horrible smell, and is resolved by dilute acids into tertiary butylamine and formic acid.

Tertiary butylphenylamine, $\text{CMe}_3\cdot\text{NHPh}$, obtained from tertiary butyl iodide and aniline, boils at $208\text{--}210^\circ$.

Benzyl nitrate, $\text{CH}_2\text{Ph}\cdot\text{O}\cdot\text{NO}_2$, prepared from benzyl chloride and silver nitrate, boils at 106° under 20 mm. pressure, and decomposes explosively at 180 — 200° ; it behaves towards ethyl sodiomalonate and ethyl sodioacetoacetate like benzyl chloride, and yields dimethylbenzylammonium nitrate with dimethylaniline. M. O. F.

Disulphones. III. Mercaptols and Disulphones of Ketonic Acids, and Unsaturated Acids derived therefrom. By THEODOR POSNER (*Ber.*, 1899, 32, 2801—2815).—Ethyl pyruvate condenses with ethyl mercaptan in presence of hydrogen chloride to form *ethyl α -diethiothiopropionate (ethyl pyruvate ethylmercaptole)*, $\text{CMe}(\text{SEt})_2\cdot\text{CO}_2\text{Et}$, a yellow oil which is oxidised by aqueous potassium permanganate to *ethyl α -diethyldisulphonepropionate (ethyl pyruvate diethyl disulphone)*, $\text{CMe}(\text{SO}_2\text{Et})_2\cdot\text{CO}_2\text{Et}$; this crystallises from 50 per cent. alcohol in long, colourless needles, melts at 60 — 62° , and on hydrolysis with boiling 10 per cent. sodium hydroxide does not give rise to the corresponding acid, but loses carbon dioxide and yields diethylethylidenedisulphone, $\text{CHMe}(\text{SO}_2\text{Et})_2$ which melts at 75 — 76° , not at 60° , as stated by Escales and Baumann (*Abstr.*, 1887, 123).

Ethyl β -diethiothiobutyrate (ethyl acetoacetate ethylmercaptole), $\text{CMe}(\text{SEt})_2\cdot\text{CH}_2\cdot\text{CO}_2\text{Et}$, prepared by passing hydrogen chloride through a mixture of ethyl mercaptan and ethyl acetoacetate, is a colourless oil with a penetrating odour; it boils at 137 — 138° under 37 mm. pressure, has a sp. gr. 1.0341 at $16^\circ/13^\circ$, n_D 1.5092 at 15° , and molecular refraction 86.652. It is only slowly hydrolysed by boiling 10 per cent. aqueous caustic soda, giving rise apparently to *β -diethiothiobutyric acid (acetoacetic acid ethylmercaptole)*, $\text{CMe}(\text{SEt})_2\cdot\text{CH}_2\cdot\text{CO}_2\text{H}$, but on attempting to crystallise this, ethyl mercaptan is evolved and *β -ethiothioisocrotonic acid*, $\text{SEt}\cdot\text{CMe}\cdot\text{CH}\cdot\text{CO}_2\text{H}$, melting at 90 — 91° , formed; the latter is probably identical with the acid obtained by Autenrieth (*Abstr.*, 1890, 361) by the interaction of β -chloroisocrotonic acid with sodium ethylmercaptide, but the barium salt crystallises with $2\text{H}_2\text{O}$, instead of 1, as stated by that author; the *ethyl* ester boils at 195° .

Ethyl β -diethiothio- α -methylbutyrate (ethyl methylacetoacetate ethylmercaptole), $\text{CMe}(\text{SEt})_2\cdot\text{CHMe}\cdot\text{CO}_2\text{Et}$, prepared from ethyl methylacetoacetate, boils at 132° under 39 mm., and at 125° under 29 mm. pressure, and possesses a characteristic odour; it has a sp. gr. 1.0531 at $15^\circ/13^\circ$, n_D at 15° 1.51326, molecular refraction 89.662. On hydrolysis with sodium hydroxide, it yields *β -diethiothio- α -methylbutyric acid (methylacetoacetic acid ethylmercaptole)*, $\text{CMe}(\text{SEt})_2\cdot\text{CHMe}\cdot\text{CO}_2\text{H}$, a white powder which, on crystallising from water or acetic acid, is converted into *β -ethiothio- α -methylisocrotonic acid (thioethylangelic acid)*, $\text{SEt}\cdot\text{CMe}\cdot\text{CMe}\cdot\text{CO}_2\text{H}$, which separates in white leaflets, melts at 99 — 101° , and yields a crystalline barium salt, $(\text{C}_7\text{H}_{11}\text{O}_2\text{S})_2\text{Ba} + 2\text{H}_2\text{O}$, and an *ethyl* ester boiling at 192 — 194° .

Ethyl- β -diethiothio- α -ethylbutyrate (ethyl ethylacetoacetate ethylmercaptole), $\text{CMe}(\text{SEt})_2\cdot\text{CHEt}\cdot\text{CO}_2\text{Et}$, prepared from ethyl ethylacetoacetate, boils at 152° under 49 mm., and at 138° under 39 mm. pressure, has a sp. gr. 1.0077 at $16^\circ/13^\circ$, n_D 1.49394, molecular refraction 94.70; it is hydrolysed by caustic soda only with difficulty, and is then converted

into β -ethothio- α -ethylisocrotonic acid, $\text{SEt} \cdot \text{CMe} \cdot \text{CEt} \cdot \text{CO}_2\text{H}$, without yielding any intermediate compound; the acid crystallises from methyl alcohol in slender, colourless needles, melts at $64-65^\circ$, and yields a barium salt, $(\text{C}_8\text{H}_{13}\text{O}_2\text{S})_2\text{Ba} + 2\text{H}_2\text{O}$.

When hydrogen chloride is passed into a solution of lævulic acid and ethyl mercaptan in glacial acetic acid, γ -diethothiovaleric acid (lævulic acid ethylmercaptole), $\text{CMe}(\text{SEt})_2 \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{CO}_2\text{H}$, is obtained as a colourless oil; the ethyl ester, $\text{CMe}(\text{SEt})_2 \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{CO}_2\text{Et}$, can be prepared similarly from ethyl lævulate. On oxidising the acid with cold aqueous potassium permanganate, γ -diethyldisulphonevaleric acid (lævulic acid diethyldisulphone), $\text{CMe}(\text{SO}_2\text{Et})_2 \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{CO}_2\text{H}$, is obtained; it crystallises from alcohol in monoclinic plates, melts at 140° , and yields an ill-characterised barium salt, with $+4\text{H}_2\text{O}$, and an ethyl ester, $\text{C}_9\text{H}_{18}\text{O}_6\text{S}_2$, which separates from dilute alcohol in large crystals and melts at $96-96.5^\circ$; the latter is easily hydrolysed to the corresponding acid, without decomposing to form an unsaturated acid, as in the case of the disulphones of β -ketonic acids. The diethylamide, $\text{CMe}(\text{SO}_2\text{Et})_2 \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{CO} \cdot \text{NEt}_2$, crystallises from water in colourless plates and melts at 101° ; the *p*-phenetidine and the piperidide crystallise from dilute alcohol in colourless needles, melt at 136° and 171° respectively, and do not appear to possess any decided physiological activity.

β -Diethothioglutaric acid (acetonedicarboxylic acid ethylmercaptole, $\text{C}(\text{SEt})_2(\text{CH}_2 \cdot \text{CO}_2\text{H})_2$), obtained by the slow condensation of acetonedicarboxylic acid and ethyl mercaptan at 0° , crystallises from dilute alcohol in large, transparent, monoclinic crystals, and melts at $140-141^\circ$; the diethyl ester, $\text{C}(\text{SEt})_2(\text{CH}_2 \cdot \text{CO}_2\text{Et})_2$, prepared from ethyl acetonedicarboxylate, is a nearly colourless oil with a penetrating odour; it boils at 192° under 30 mm. pressure, has a sp. gr. 1.1012 at $17^\circ/13^\circ$, n_D at 15° 1.5051, molecular refraction 100.21. On hydrolysis with 20 per cent. aqueous caustic soda, this does not yield the corresponding acid, but in like manner to the derivatives of β -ketonic acids, gives rise to ethyl mercaptan and β -ethothioglutaconic acid, $\text{CO}_2\text{H} \cdot \text{CH}_2 \cdot \text{C}(\text{SEt}) \cdot \text{CH} \cdot \text{CO}_2\text{H}$, which crystallises from alcohol in monoclinic prisms and melts and decomposes at $155-163^\circ$; the same compound is also formed by the interaction of acetonedicarboxylic acid and ethyl mercaptan in presence of hydrogen chloride if the mixture is not kept thoroughly cool; the copper salt, $\text{C}_7\text{H}_8\text{O}_4\text{SCu}$, the silver salt, $\text{C}_7\text{H}_8\text{O}_4\text{SAg}_2$, and the barium salt, $\text{C}_7\text{H}_8\text{O}_4\text{SBa} + \text{H}_2\text{O}$, were prepared. Ethyl β -diethyldisulphoneglutarate (ethyl acetonedicarboxylate diethyldisulphone), $\text{C}(\text{SO}_2\text{Et})_2(\text{CH}_2 \cdot \text{CO}_2\text{Et})_2$, obtained by oxidising the corresponding mercaptole with aqueous potassium permanganate, crystallises from 50 per cent. alcohol in slender, white needles, and melts at 104° ; on hydrolysis with 10 per cent. aqueous sodium hydroxide, it yields ethylsulphinic acid, ethyl alcohol, and β -ethylsulphoneglutaconic acid, $\text{CO}_2\text{H} \cdot \text{CH}_2 \cdot \text{C}(\text{SO}_2\text{Et}) \cdot \text{CH} \cdot \text{CO}_2\text{H}$, which forms slender needles and melts at $175-177^\circ$. This behaviour is similar to that of the esters of β -disulphonecarboxylic acids on hydrolysis (Autenrieth, Abstr., 1891, 1067); an attempt to obtain β -diethylsulphoneglutarate by carefully oxidising the corresponding mercaptole failed.

W. A. D.

Resolution of Racemic Compounds into their Active Components. By PAUL WALDEN (*Ber.*, 1899, 32, 2703—2706. Compare Marckwald and McKenzie, *Abstr.*, 1899, ii, 733).— α -Bromopropionyl bromide, when treated with $\frac{1}{2}$ mol. of *l*-amyl alcohol, gives an amyl bromopropionate which has $\alpha_D + 3.20^\circ$, in a 10 cm. tube, whilst when 4 mols. are used, the rotation is $\alpha_D + 2.99^\circ$; in the former case, it is supposed that the ester of the racemic bromopropionic acid is mixed with a certain amount of that of the *d*-acid, showing that the acid had been partially resolved by fractional esterification. Similarly, silver methylsuccinate with $\frac{1}{3}$ mol. of active amyl iodide gave an ester which has $\alpha_D + 1.50^\circ$ in a 10 cm. tube, whilst with an excess of the iodide $\alpha_D + 3.50$ is obtained; in the former case, it is supposed that the product contained an excess of the ester of the *l*-acid, a conclusion which was confirmed by the fact that on hydrolysis an alkaline solution of methylsuccinic acid was obtained which showed a very slight levorotatory power. T. M. L.

Affinity Coefficients of Saturated Fatty Acids. By JEAN BILLITZER (*Monatsh.*, 1899, 20, 666—678).—The conductivity of a number of fatty acids has been determined in order to see what influence structure has on the relative strength.

The following are the constants for the valeric acids:

	Normal valeric acid.	Isovaleric acid.	α -Methyl- butyric acid.	$\alpha\alpha$ -Dimethyl- propionic acid.
Boiling point.	186°	176°	177°	164°
Solubility at 25°	1:23.8	1:19.6	1:20.4	1:43.2
Specific gravity at 25°	0.9379	0.926	0.9433	(at 50°) 0.905
Specific volume at 25°	108.77	110.1	108.14	(at 50°) 111.5
Conductivity.....	0.00161	0.00173	0.00168	0.000978

The ratio of the conductivities corresponds neither with that of the boiling points nor yet with that of the specific volumes. The constants obtained by the inversion of sugar by these acids are in the same ratio, namely: 1:1.15:1.08:0.65.

The conductivity of normal butyric acid is 0.00154, of isobutyric acid, 0.00162, of normal hexoic acid, 0.00146, of isohexoic acid, 0.00153, of α -ethylpropionic acid, 0.00203, of $\alpha\alpha$ -dimethylpropionic acid, 0.000957.

From these results, it would appear that in a "series of isomeric acids, the conductivity depends on the proximity of the hydrogen atoms to the carboxylic group." R. H. P.

Water of Crystallisation in the Calcium and Barium Salts of γ -Methylvaleric (Isohexoic) Acid. By FRITZ ORNSTEIN (*Monatsh.*, 1899, 20, 661—665).—Saturated solutions of calcium and barium isohexoates were shaken with an excess of the salts at different constant temperatures for about 2 hours. The undissolved salt was then filtered off, quickly pressed, and analysed. The calcium salt at 0° and 13° contains 5H₂O, at 20°, 40°, and 52° 3½H₂O, and at 80° only 2H₂O. Similarly, the barium salt at 0°, 13°, 30°, 60°, and 80° contains respectively 4, 4, 3, 2½, and 2H₂O. R. H. P.

Mixed Anhydrides of Acyclic and Cyclic Acids. By AUGUSTE BÉHAL (*Compt. rend.*, 1899, 129, 681—684. Compare Abstr., 1899, i, 734).—Acetic isovaleric anhydride, prepared by Gerhardt's or Autenrieth's method (Abstr., 1888, 250), is never quite pure, because it is slowly decomposed by the liquid used in washing it; if the washing is continued, it is finally completely decomposed, leaving isovaleric anhydride.

A solution of 1 mol. of benzoic anhydride in 1 mol. of acetic anhydride is rapidly decomposed in the cold by an aqueous solution of sodium carbonate, leaving the benzoic anhydride unchanged. A solution of sodium carbonate has very little action on acetic benzoic anhydride. This proves that mixed anhydrides are compounds, and not mixtures, as supposed by Rousset (Abstr., 1895, i, 592).

When molecular quantities of acetic anhydride and benzoic anhydride are boiled for 3 hours, 30 per cent. of the mixture is converted into the mixed anhydride. If the heating is continued, the amount of mixed anhydride does not increase, but diminishes slightly. This accounts for the presence of free benzoic anhydride in acetic benzoic anhydride.

When acetic benzoic anhydride or acetic isovaleric anhydride is treated with ammonia, the amide formed is that of the acid which contains the least amount of carbon. This is in direct contradiction to Autenrieth's statement.

When mixed anhydrides of acetic acid and another acid are treated with phenylhydrazine, the hydrazone of acetic acid is always formed.

When molecular quantities of an alcohol and a mixed anhydride are heated together, the ester formed is that of the acid containing the smallest amount of carbon. A small amount of the ester of the other acid is also formed, due to the presence of the free anhydride of this acid. Hydrochloric acid decomposes mixed anhydrides, with formation of the chloride of the acid containing the smaller amount of carbon.

H. R. LE S.

Vinylacetic Acid. By FRITZ FIGHTER and ALBERT KRAFFT (*Ber.*, 1899, 32, 2799—2800. Compare Wislicenus, Abstr., 1899, i, 736).—When von Pechmann and Jenisch's β -hydroxyglutaric acid (Abstr., 1892, 147) is distilled under diminished pressure, the chief product is an unsaturated acid, $C_4H_6O_2$, together with a small amount of glutaconic acid. The acid $C_4H_6O_2$ cannot possibly be formed by the elimination of carbon dioxide from the glutaconic acid, as this acid, when heated, yields its anhydride (Büchner, Abstr., 1894, i, 322), neither can it be formed by the elimination of water from β -hydroxybutyric acid, as this acid may be distilled under 12—14 mm. pressure without undergoing decomposition. The only other possibility is that an intermediate lactonic acid, $CO \begin{array}{c} \diagup O \\ \diagdown CH_2 \end{array} CH \cdot CH_2 \cdot CO_2H$, is formed which immediately loses water, yielding vinylacetic acid. So far, the isolation of this intermediate lactone has not been accomplished, and no direct proof of the constitution of the unsaturated acid has been obtained. It is a hygroscopic liquid boiling at 168° under atmospheric, or at 70 — 71° under 12—14 mm. pressure.

A calcium salt, $(C_4H_5O_2)_2Ca + H_2O$, is deposited from hot solutions, and this agrees with the salt described by Wislicenus (*loc. cit.*). A calcium salt containing $2H_2O$ is deposited from cold solutions, a barium salt, with $2H_2O$, and a silver salt, have also been prepared.

J. J. S.

Action of Ammonia on Lactones. By HANS MEYER (*Monatsh.*, 1899, 20, 717—733).—A critical examination of the literature of the subject, and an attempt to formulate rules for the varying action of ammonia on lactones.

In all cases where aqueous or alcoholic ammonia reacts with a lactone, an amide of a hydroxy-acid is primarily formed, but in some cases this is then transformed into an imide (lactam). The formation of these imides does not depend on the number of carbon atoms in the "lactone" ring, but on the character of the carbon atom to which is attached the hydroxyl group of the corresponding hydroxy-acid. An imide is formed when this carbon atom is (i) tertiary, (ii) secondary and unsaturated. When the hydroxyl group attached to this carbon atom forms (i) a primary alcohol, (ii) a secondary saturated alcohol, or (iii) a phenol, the amide of a hydroxy-acid is formed.

R. H. P.

α -Hydroxy- α -methylisohexylacetic [**α -Hydroxy- α -dimethylheptioic**] Acid. By KARL AUWERS (*Ber.*, 1899, 32, 2573—2575).—Auden, Perkin and Rose (*Trans.*, 1899, 75, 909) have prepared α -hydroxy- β -isoamylisobutyric acid, melting at 76° [not 66° , as quoted by the author], by hydrolysing the compound obtained by the interaction of hydrogen cyanide and isoamylacetone. In conjunction with J. Reis (*Inaug. Diss. Heidelberg*, 1897), the author prepared the same acid in the same way and called it α -methyl- α -hydroxy-isohexylacetic acid. The methyl ester, $C_{10}H_{20}O_3$, is a colourless, mobile liquid with a pleasant, fruity smell and boils at 215° under ordinary pressure, and at 127° under 43 mm. pressure. Attempts to convert either the acid (or the methyl ester) into the reduction product of the campholytic acids by elimination of water were unsuccessful as unsaturated compounds were invariably obtained.

T. H. P.

Influence of the Solvent on the Constitution of Ethyl Acetoacetate and similar Substances. By WILHELM WISLICENUS (*Ber.*, 1899, 32, 2837—2840. Compare *Abstr.*, 1896, i, 553).—Solutions of ethyl formylsuccinate, ethyl formylphenylacetate, ethyl formylmalonate, ethyl α -phenylacetoacetate, and ethyl acetoacetate in methyl alcohol, ethyl alcohol, ether, or benzene were kept until a state of equilibrium between the enolic and ketonic (or aldehydic) forms had been reached. In order to compare the amount of the enolic form present in different solvents, each solution was diluted with alcohol, and the colour developed by a drop of ferric chloride solution was compared with that produced in a standard alcoholic solution. It was found that, in all cases, the amount of the enolic form was greatest in benzene and least in methyl alcohol, but that the influence of the solvent, which was very great in the case of ethyl formylsuccinate and ethyl formylphenylacetate, was much less marked in the case of the

other three esters. Quantitative measurements of the colour intensity are given in the paper. T. M. L.

β -Bromoglutaric Acid. By W. SSEMENOFF (*Chem. Centr.*, 1899, ii, 28—29; from *J. Russ. Chem. Soc.*, 1899, 31, 386—394. Compare Abstr., 1899, i, 1070).—Only small yields of glutaconic acid are obtained from ethyl sodiodicarboxylglutaconate by Conrad and Guthzeit's method, but von Pechmann and Jenisch's method (Abstr., 1892, 147; compare Bolam, *Proc.*, 1896, 184) with slight modifications proved satisfactory. By the action of hydrobromic acid on glutaconic acid, β -bromoglutaric acid, $\text{CHBr}(\text{CH}_2 \cdot \text{CO}_2\text{H})_2$, alone is formed. The crystalline mass so obtained contained crystals of different forms, but they all melted at 139—140, and contained about $\frac{3}{8}\text{H}_2\text{O}$. By boiling β -bromoglutaric acid with a solution of sodium carbonate ($1\frac{1}{2}$ mols.), 80 per cent. of β -hydroxyglutaric acid, $\text{OH} \cdot \text{CH}(\text{CH}_2 \cdot \text{CO}_2\text{H})_2$, and a volatile, monobasic, unsaturated acid, $\text{CH}_2 \cdot \text{CH} \cdot \text{CH}_2 \cdot \text{CO}_2\text{H}$, are formed (compare Abstr., 1899, 866 and 867). The properties of the latter are not those of vinylacetic acid, and the calcium and barium salts prepared from it are not identical with the known barium and calcium crotonates. E. W. W.

Esterification of Camphoric Acid. II. By RUDOLF WEGSCHEIDER (*Monatsh.*, 1899, 20, 685—697).—The author has prepared the alkyl salts of camphoric acid by the action of the alkyl haloids on the potassium hydrogen salt and by the action of sodium ethoxide in the presence of benzene on camphoric anhydride. The methyl hydrogen salts were also prepared by Walker's method (*Trans.*, 1892, 51, 1088). A mixture of the two alkyl hydrogen salts is very difficult to separate; the separation is, however, partly successful, if the salts are treated with a very dilute solution of copper sulphate, which precipitates the "ortho"-salt only.

When potassium hydrogen camphorate is treated with methyl iodide in methyl alcoholic solution, there is formed a mixture of the "ortho"- and "allo"-methyl hydrogen salts with some of the dimethyl ester. The same products are obtained by the action of sodium methoxide on camphoric anhydride.

These results are not contrary to the author's rule for the esterification of dibasic acids (Abstr., 1895, ii, 310), since it can be assumed that the affinity constants of the two carboxylic groups do not differ much. Also the reactions do not run smoothly, since the dialkyl esters are formed at the same time. The formation of both methyl hydrogen salts by the action of sodium methoxide on camphoric anhydride is in accordance with the author's views (Abstr., 1898, i, 30). R. H. P.

Behaviour of Malic Acid when Heated. By PAUL WALDEN (*Ber.*, 1899, 32, 2706—2721. Compare Aberson, Abstr., 1898, i, 513).—When *l*-malic acid is heated at 100° during 24 hours, or at 160° in a vacuum during 20 minutes, it is converted into an amorphous tribasic *anhydromalic acid*, $\text{C}_5\text{H}_7\text{O}_5(\text{CO}_2\text{H})_3$, which is regarded as a malomalic acid formed by elimination of water between the CO_2H group of one molecule and the OH of another. When pre-

pared at 100° , the acid has $[\alpha]_D -18.8^{\circ}$ in acetone and -14.0° in water, but when prepared at 160° , -21.4 in acetone and -16.2° in water. The anhydro-acid is reconverted into *l*-malic acid when heated with water in sealed tubes. When a solution in methyl alcohol is saturated with hydrogen chloride, or when the silver salt is treated with methyl iodide, dimethyl *l*-malate is produced, together with an ester, $C_{10}H_{12}O_8$, melting at $101-102^{\circ}$, and probably identical with that described by Aberson.

On heating to a higher temperature in a vacuum during a longer period, an anhydride, $C_8H_8O_8$, is produced which appears to be identical with Aberson's malide from the malic acid of *Crassulaceæ*.

All the reactions of malic acid from *Crassulaceæ* described by Aberson are given by malic acid from mountain ash berries, and the two acids only differ in that Aberson's acid is dextrorotatory; the nature of the isomerism is not yet understood. T. M. L.

Optical Rotation of Malic Acid in the Pure State and in Solution. By PAUL WALDEN (*Ber.*, 1899, 32, 2849—2862).—The existence of a third optically active malic acid, obtained by Aberson from *Crassulaceæ* (*Abstr.*, 1898, i, 513), would necessitate an extension or abandonment of prevailing stereochemical views. In general chemical behaviour, this new modification is extremely similar to ordinary malic acid (compare preceding abstract), and the only real difference is in the amount and direction of the rotation. This being so, the author has investigated thoroughly the rotatory behaviour of natural malic acid.

At 20° , dilute solutions of malic acid are lævorotatory; a 34.24 per cent. solution is inactive, and still more concentrated solutions are dextrorotatory, converging on the value $[\alpha]_D +5.89$ at 22° for the pure acid; natural malic acid is accordingly regarded as a dextrorotatory substance at ordinary temperatures.

Active malic acid has a relatively low melting point (100°) and can readily be undercooled, allowing a measurement of the rotation at lower temperatures. Crystallised and dried malic acid was kept for 10 minutes at $100-110^{\circ}$, and had then its rotation determined, light of various wave-lengths being used. At $90-95^{\circ}$, for a tube length of 100 mm., $\alpha_D -5.5^{\circ}$, at 17° after slow cooling $\alpha_D +5.2^{\circ}$. These values, however, were obtained only when the acid was heated for a short time at 100° . When the heating lasted 30 minutes (*A*), α_D had the following values: -5.0° (*l* 100 mm.) at 50° , -1.0° at 43° , $+0.5^{\circ}$ at 36° , $+3.0^{\circ}$ at 28° . When the heating lasted $6\frac{1}{2}$ hours (*B*), in the course of which there was no loss of weight, $\alpha_D -12^{\circ}$ at about 70° , -5.1° at 20° . A third specimen (*C*), heated for $14\frac{1}{2}$ hours, gave $\alpha_D -13^{\circ}$ at about 60° , and after cooling for 2 hours in a desiccator, $+43^{\circ}$ at 20° . The same three specimens in acetone solution gave for $[\alpha]_D -8.1^{\circ}$, -13.8° , and -16.2° respectively, whilst dried malic acid (not previously fused) gave in acetone solution $[\alpha]_D -7.0^{\circ}$; thus the lævorotation increases with the duration of the heating.

These changes can be accounted for either by the formation of a new isomeric malic acid, such as that of Aberson, or by a partial dehydration, $2CO_2H \cdot CH(OH) \cdot CH_2 \cdot CO_2H$, passing into $C_5H_7O_3(CO_2H)_3$.

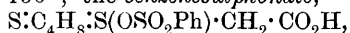
In the former case, the molecular weight and the acidity ought to be the same as those of ordinary malic acid; in the latter case, the molecular weight should be greater and the acidity less. Determinations of the molecular weight in acetone solution by the boiling point method gave for the unchanged malic acid M 150—151, for A 158—164, for B 190—196, and for C 190—198°. Equally concentrated solutions of A , B , and C required gradually decreasing quantities of barium hydroxide for neutralisation. These observations are opposed to the assumption of a new modification of malic acid, and are well accounted for by a partial dehydration.

The rotation of natural malic acid has also been determined in numerous pure and mixed organic solvents, such as benzyl alcohol, formic acid, phenyl methyl ketone, isobutyl alcohol, acetaldehyde, and pyridine. The values obtained for $[\alpha]_D$ in these solutions vary from $+4.0^\circ$ to -30.0° , and hence no conclusion can be drawn as to the characteristic malic acid rotation. Comparison, however, of the malic acid ion, for which $[\alpha]_D - 14^\circ$ to -11° , with the malic acid esters, for which $[\alpha]_D - 7^\circ$ to -12° , makes it tolerably certain that $[\alpha]_D$ for the free malic acid molecule has a value of about -10° . This principle of reasoning is supported by the rotations of *l*-mandelic acid (with *l*-ævrotatory ion and esters), the tartaric acids, the active chlorosuccinic acids, and others. The principle, if accepted, would point to sarcosuccinic acid, commonly called dextrorotatory, being really *l*-ævrotatory. Similarly, *d*-glyceric acid, which yields a *l*-ævrotatory ion and *l*-ævrotatory esters, would have to be regarded as really *l*-ævrotatory.

Discussion of the causes of the varying amount and direction of the malic acid rotation is reserved for a later paper. J. C. P.

Diethylenedisulphidethetine. By DANIEL STRÖMHOLM (*Ber.*, 1899, 32, 2892—2911. Compare *Abstr.*, 1898, i, 625).—*Diethylene-disulphidethetine bromide*, $S\begin{smallmatrix} \text{CH}_2 \cdot \text{CH}_2 \\ \text{CH}_2 \cdot \text{CH}_2 \end{smallmatrix} \text{SBr} \cdot \text{CH}_2 \cdot \text{CO}_2\text{H}$, obtained by heating together diethylene disulphide and monobromoacetic acid, crystallises in prisms melting at 159° ; it is readily soluble in hot water, but sparingly in cold water and alcohol. Its solution is acid and has a bitter taste; when boiled for some time, the dissolved substance undergoes a partial dissociation into its generators. *Diethylene-disulphidethetine*, $S:C_4H_8:S\begin{smallmatrix} \text{CH}_2 \\ \text{O} \end{smallmatrix} \text{CO}$, produced by shaking the bromide with silver oxide, crystallises from water or alcohol in white needles containing $2H_2O$; it melts at $108-109^\circ$. It retains its water of crystallisation very tenaciously, and only parts with it in a vacuum desiccator; a portion of the dehydrated thetine acts catalytically on the hydrated substance, so that the latter, when mixed with the former, readily loses water even in an ordinary desiccator. The anhydrous thetine forms lustrous, white scales which decompose at about 130° . The compound $(C_6H_{10}O_2S_2)_2 \cdot HBr$, obtained by mixing together the thetine and its bromide in molecular proportion, separates in hard crystals and melts at 179° . The calcium and barium salts, $(S:C_4H_8:SBrCH_2 \cdot CO_2)_2R$, crystallise in leaflets with

$5\text{H}_2\text{O}$ and $4\text{H}_2\text{O}$ respectively. *Diethylenedisulphidethetine chloride* resembles the bromide and melts and decomposes at 167° ; the *calcium* derivative crystallises with $5\text{H}_2\text{O}$. Ferric chloride gives a yellowish-brown precipitate with the thetine, but the product appears to be a mixture. *Diethylenedisulphidethetine iodide* forms white prisms melting at 130° ; the *barium* derivative crystallises with $4\text{H}_2\text{O}$; the *hydrogen sulphate* forms well-defined crystals; the *nitrate* crystallises in leaflets containing $1\text{H}_2\text{O}$, which melt at 109° and the anhydrous compound melts at 130° ; the *benzenesulphonate*,



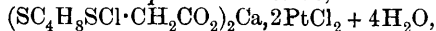
forms well-defined plates melting at 171° ; the *trichloroacetate* melts at 91° , and its *barium* salt crystallises in prisms with $5\text{H}_2\text{O}$, the benzoate, tartrate, and phosphates could not be obtained in a solid form; the *picrate* crystallises in tufts of yellow needles and melts at 149° ; the *fluoride* crystallises from a solution of hydrofluoric acid with $2\text{H}_2\text{O}$; when heated to 80° , it loses $1\text{H}_2\text{O}$; the *acetate* crystallises with $\frac{1}{2}\text{H}_2\text{O}$, and loses this water when left in a desiccator; the anhydrous salt melts at $116\text{--}117^\circ$.

Vinylthioethylenethioglycollic acid, $\text{CH}_2:\text{CH}\cdot\text{S}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{S}\cdot\text{CO}_2\text{H}$, is obtained as an oil, together with a solid polymeride melting at 122° , by evaporating to dryness an alkaline solution of the thetine and liberating the products by adding a mineral acid; the *potassium* salts and *barium* salts are described.

The *platinichloride*, $\text{PtCl}_4\cdot\text{S}:\text{C}_4\text{H}_8:\text{SCl}\cdot\text{CH}_2\cdot\text{CO}_2\text{H}$, is obtained as a yellow, amorphous precipitate on mixing solutions of platinic chloride and thetine chloride; it dissolves in caustic soda.

The salt, $(\text{S}:\text{C}_4\text{H}_8:\text{SCl}\cdot\text{CH}_2\cdot\text{CO}_2\text{K})_2\text{PtCl}_2$, is produced by evaporating nearly to dryness an aqueous solution of thetine (2 mols.) and potassium platinosochloride (1 mol.); the oily residue is treated with alcohol, when a semicrystalline, brownish-yellow mass separates, which is pressed and dried. When allowed to remain for some time in a desiccator, this substance is converted into a yellow mass which contains no potassium; the same compound, $(\text{S}:\text{C}_4\text{H}_8:\text{S}\langle\text{CH}_2\rangle\text{CO})_2\text{PtCl}_2$, is also formed by allowing the solution of thetine and potassium platinosochloride to remain at the ordinary temperature, or by heating it for some time on a water-bath.

Calcium thetineplatinichloride, $(\text{C}_6\text{H}_{10}\text{S}_2\text{O}_2)_2\text{CaPtCl}_6$, crystallises with $2\frac{1}{2}\text{H}_2\text{O}$; the *calcium thetine platinosochloride*,



separates in aggregates of red crystals.

Oxydiethylenedisulphidethetine bromide, $\text{SO}:\text{C}_4\text{H}_8:\text{SBr}\cdot\text{CH}_2\cdot\text{CO}_2\text{H}$, is prepared by heating an aqueous solution of diethylenedisulphidethetine bromide and bromine (1 mol.) on a water-bath, and then concentrating over concentrated sulphuric acid; it crystallises in plates, melts at $158\text{--}159^\circ$, and is readily soluble in water.

Oxydiethylenedisulphidethetine, $\text{SO}:\text{C}_4\text{H}_8:\text{S}\langle\text{CH}_2\rangle\text{CO} + \text{H}_2\text{O}$, crystallises in hard plates and melts at 133° ; it retains its water of crystallisation in a desiccator. The *platinichloride* crystallises, with $4\frac{1}{2}\text{H}_2\text{O}$, in rosettes of lustrous, orange prisms.

When an excess of bromine is added to an aqueous solution of oxydiethylenedisulphidethetine bromide, an unstable dibromo-derivative, $\text{SO}:\text{C}_4\text{H}_8:\text{SBr}\cdot\text{CBr}_2\cdot\text{CO}_2\text{H}$, is probably formed, and this, on heating the solution, decomposes into carbon dioxide and *oxydiethylenedisulphidedibromomethylsulphine bromide*, $\text{SO}:\text{C}_4\text{H}_8:\text{SBr}\cdot\text{CHBr}_2$; this crystallises in aggregates of prisms or needles and melts at 135° ; the *chloride* melts at 156° and yields a sparingly soluble *platinichloride*. The *nitrate* is, unlike the halogen salts, very soluble.

Dimethyldibromomethylsulphine bromide is the final product of the action of bromine on aqueous solutions of dimethylthetine bromide; it crystallises from water in well-defined, hexagonal plates and melts at $120\text{--}121^\circ$; the *platinichloride* crystallises in needles.

Dimethyldichloromethylsulphine platinichloride, $\text{C}_6\text{H}_{14}\text{Cl}_{10}\text{S}_2\text{Pt}$, crystallises in lustrous scales.
G. T. M.

History of Thioacetaldehydes. By EMIL FROMM (*Ber.*, 1899, 32, 2650—2653. Compare Klinger, *Abstr.*, 1899, i, 859).—Priority as regards the preparation of trithioacetaldehydes, and also as regards their constitution, is conceded to Klinger, but this author's statement that Baumann and Fromm have brought forward no fresh evidence in support of the constitution of these compounds is incorrect. The formation of trisulphones is certainly an argument in favour of the cyclic formula.

Klinger's "alloergatia" theory is criticised.

J. J. S.

Action of Nitrosyl Chloride on Organic Compounds containing a Double Linking. By WLADIMIR IPATIEFF (*Chem. Centr.*, 1899, ii, 176—178; from *J. Russ. Chem. Soc.*, 1899, 31, 426—441).—The action of nitrosyl chloride on compounds containing the group $:\text{C}:\text{CH}\cdot$, $\cdot\text{CH}:\text{CH}\cdot$, or $\cdot\text{CH}:\text{CH}_2$ respectively has been investigated. In accordance with Wallach's results, compounds of the first class were found to yield solid products. By adding fuming hydrochloric acid drop by drop to a cooled solution of δ -methyl- Δ^7 -amylene (*Abstr.*, 1899, i, 469) in amyl nitrite and allowing the mixture to remain 24 hours, the mass solidifies and *ethylchlorisopropylketoxime*, $\text{CMe}_2\text{Cl}\cdot\text{CEt}\cdot\text{NOH}$, is obtained; it crystallises from benzene or ethyl acetate in colourless prisms, melts at $77\text{--}78^\circ$, and is readily soluble in benzene. *Chlorodiethylacetoxime*, $\text{CEt}_2\text{Cl}\cdot\text{CMe}\cdot\text{NOH}$, prepared by the action of nitrosyl chloride on γ -ethyl- Δ^2 -amylene crystallises from hot ethyl acetate in prisms and melts at $57\text{--}59^\circ$. *Chloromethylethylacetoxime*,

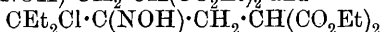
$\text{CMeEtCl}\cdot\text{CMe}\cdot\text{NOH}$,

obtained similarly from γ -methyl- Δ^2 -amylene, melts at $66\text{--}67^\circ$. Since diamylene, like Δ^2 -hexylene, when treated with nitrosyl chloride, does not form a solid product, it probably does not contain the group $:\text{C}:\text{C}:$ or $:\text{C}:\text{CH}\cdot$ (compare Butlerow, *J. Russ. Chem. Soc.*, 9, 76). The Δ^2 -hexylene (*Annalen*, 1865, 135, 141) contained a small quantity of butylethylene (Wagner, *Diss.*). Diamylene, prepared by the action of sulphuric acid on dimethylethylcarbinol, boils at $154\text{--}156^\circ$.

[With A. SOLONINA].—By the action of nitrosyl chloride on isoamylene (γ -methyl- Δ^2 -butylene) prepared by Wischnegradski's method by the action of an alcoholic solution of an alkali on fermentation amyle iodide, only liquid products are formed.

Action of nitrosyl chloride on disubstituted ethyl allyl ethers. The ketonic alcohol, $\text{CMe}_2\text{Cl}\cdot\text{C}(\text{NOH})\cdot\text{CH}_2\cdot\text{OEt}$, prepared from ethyl dimethylallyl ether, separates from ethyl acetate in colourless crystals and melts at $79.5\text{--}80.5^\circ$. Ethyl diethylallyl ether forms the compound $\text{CEt}_2\text{Cl}\cdot\text{C}(\text{NOH})\cdot\text{CH}_2\cdot\text{OEt}$, which crystallises in colourless prisms and melts at $88\text{--}89^\circ$. From ethyl methylethylallyl ether, the compound $\text{CMeEtCl}\cdot\text{C}(\text{NOH})\cdot\text{CH}_2\cdot\text{OEt}$ is obtained; it melts at $67\text{--}69^\circ$.

Action of nitrosyl chloride on disubstituted ethyl allylmalonates. Ethyl dimethylallylmalonate and ethyl diethylallylmalonate form the compounds $\text{CMe}_2\text{Cl}\cdot\text{C}(\text{NOH})\cdot\text{CH}_2\cdot\text{CH}(\text{CO}_2\text{Et})_2$ and



respectively. The former crystallises from benzene in prisms and melts at $85\text{--}87^\circ$; the latter crystallises from ethyl acetate in prisms and melts at $94\text{--}96^\circ$.

All the preceding compounds, after boiling with hydrochloric acid, reduce Fehling's solution. Crystalline chloroisosnitroso-compounds are thus only obtained from compounds which contain the group $\text{:C:CH}\cdot$, and this also applies to the terpenes. The action of nitrosyl chloride is characteristic and requires little material. E. W. W.

Electrolysis of Solutions of Sucrose. By KARL ULSCH (*Zeit. Elektrochem.*, 1899, 5, 539—541).—Dilute solutions of sucrose in moderately concentrated solutions of sulphuric acid, or potassium or barium hydroxide, are electrolysed at various temperatures, using platinum electrodes. With sulphuric acid alone, it is not possible to oxidise the sugar completely to carbon dioxide, but in presence of manganous sulphate the oxidation may reach 98 per cent. With potassium hydroxide, over 96 per cent. of the theoretical amount of carbon dioxide was obtained. With barium hydroxide at 80° , the oxidation was fairly complete in about 4 hours, and was very readily made quantitative by acidifying and adding potassium permanganate, which was not the case with the solutions in sulphuric acid or potassium hydroxide. T. E.

Methylene-glucose from Glucose, Formaldehyde, and Hydrochloric Acid: A New Glucoside. By BERNHARD TOLLENS (*Ber.*, 1899, 32, 2585—2588).—*Methylene-glucose*, $\text{CH}_2\cdot\text{C}_6\text{H}_{10}\text{O}_6 + \frac{1}{2}\text{H}_2\text{O}$, is obtained by allowing a mixture of dextrose, 40 per cent. formaldehyde solution, and hydrochloric and acetic acids to remain for some months with occasional shaking; it crystallises from water in white needles and becomes anhydrous when dried at 100° ; it melts at $187\text{--}189^\circ$, sintering at $179\text{--}180^\circ$. Methylene-glucose is dextrorotatory, $[\alpha]_D +9.4^\circ$; it reduces Fehling's solution, one molecule requiring $1\frac{1}{2}$ atoms of oxygen, whilst one molecule of dextrose requires $2\frac{1}{2}$ atoms; unlike dextrose, it is not fermentable. The molecular weight was confirmed by cryoscopic determinations. The osazone separates from dilute alcohol as a pale yellow powder, and melts at $164\text{--}167^\circ$, sintering at $150\text{--}160^\circ$. G. T. M.

Stereochemistry of Nitrogen. By J. ACHILLE LE BEL (*Compt. rend.*, 1899, 129, 548—550).—The fact that Marckwald (*Abstr.*, 1899, i,

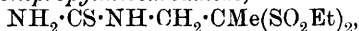
326) has been unable to confirm the author's preparation of an optically active substance by the action of moulds on the salts of methyl-ethylpropylisobutylammonium is attributed to neglect of various precautions to be observed in the preparation of this base and culture of the mould in it; full details of these are given in the paper. Repeated experiments have shown the correctness of the views put forward by the author in 1890 and 1891. N. L.

Attempts to prepare a Diaminovaleric Acid. By OSKAR EMMERLING (*Ber.*, 1899, 32, 2682—2685).—When $\gamma\delta$ -Dibromovaleric acid (Messerschmidt, *Abstr.*, 1882, 35) was heated with concentrated ammonia in a sealed tube during 6 hours at 100° , and the ammonium salt formed converted into a lead salt which was then decomposed with hydrogen sulphide, the product obtained was not $\gamma\delta$ -diaminovaleric acid, but 3-hydroxypiperidone, $\text{OH}\cdot\text{CH}\langle\begin{smallmatrix}\text{CH}_2\cdot\text{CH}_2 \\ \text{CH}_2\cdot\text{NH}\end{smallmatrix}\rangle\text{CO}$, the lactam of δ -amino- γ -hydroxyvaleric acid; it separates from alcohol in well-formed, glistening, monoclinic crystals [$a:c=1.1598:1$; $\beta=114^\circ$], melts at 145° , has a slight sweet taste, and dissolves readily in water or alcohol; it does not combine with acids and is not acted on by nitrous acid.

Barium δ -amino- γ -hydroxyvalerate is a white, hygroscopic powder; the acid could not be isolated from it, hydroxypiperidone being at once reproduced. T. M. L.

Disulphones. II. Aminosulphonals and its Derivatives and Homologues. By THEODOR POSNER and JOHANNES FAHRENHORST (*Ber.*, 1899, 32, 2749—2769. Compare also *Abstr.*, 1899, i, 604).— β -Diethyldisulphonepropylcarbamide, $\text{NH}_2\cdot\text{CO}\cdot\text{NH}\cdot\text{CH}_2\cdot\text{CMe}(\text{SO}_2\text{Et})_2$, prepared by the action of potassium cyanate on aminosulphonals hydrochloride, crystallises from hot water in small, white tablets melting at 224 — 225° , and is readily soluble in hot water, hot alcohol, or acetic acid.

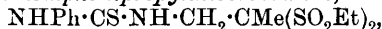
β -Diethyldisulphonepropylthiocarbamide,



forms white tablets melting at 201° , and resembles the foregoing compound in solubility.

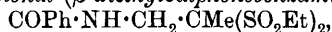
Bis- β -diethyldisulphonepropylthiocarbamide, $\text{CS}[\text{NH}\cdot\text{CH}_2\cdot\text{CMe}(\text{SO}_2\text{Et})_2]_2$, crystallises from water in felted, microscopic needles, or from alcohol in small, quadratic tablets, and melts at 159 — 161° . It is readily soluble in chloroform, acetic acid, or hot alcohol.

Phenyl- β -diethyldisulphonepropylthiocarbamide,



crystallises from dilute alcohol in slender needles melting at 173 — 174° , and dissolves readily in acetic acid, chloroform, hot alcohol, and hot benzene.

Benzoylamino-sulphonals (β -diethylsulphonebenzamide),



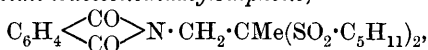
separates from hot water as an oil, which becomes crystalline when rubbed; it forms four-sided tablets with truncated angles, softens at 96° , and melts at 98 — 100° . It dissolves readily in most of the usual media with the exception of water.

γ -Chloro- β -diethiothiobutane (methyl α -chloroethylketone ethylmercaptole), $\text{CHMeCl}\cdot\text{CMe}(\text{SEt})_2$, is prepared by leading hydrogen chloride into a

cooled mixture of methyl chloroethyl ketone and ethyl mercaptan in mol. proportion; on treatment with potassium permanganate, it yields *methyl- α -chloroethylketonedithiylsulphone*, $\text{CHMeCl} \cdot \text{CMe}(\text{SO}_2\text{Et})_2$, which forms small needles, melts at $70-71^\circ$, and dissolves readily in alcohol, chloroform, and acetic acid; like methyl α -chloroethyl ketone, it does not condense with potassium phthalimide.

Chlorodithiylketonedithiylsulphone, $\text{CHMeCl} \cdot \text{CEt}(\text{SO}_2\text{Et})_2$, prepared in similar manner, forms a white mass, and melts at $47-49^\circ$.

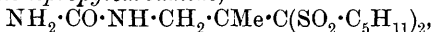
Phthaliminoacetoneamylmercaptole, $\text{C}_6\text{H}_4 \begin{smallmatrix} \text{CO} \\ \diagup \quad \diagdown \\ \text{CO} \end{smallmatrix} \text{N} \cdot \text{CH}_2 \cdot \text{CMe}(\text{S} \cdot \text{C}_5\text{H}_{11})_2$, obtained when a mixture of acetonylphthalimide and amyl mercaptan dissolved in acetic acid is saturated with hydrogen chloride, crystallises in long needles, melts at $43-44^\circ$, and dissolves readily in most of the ordinary media with the exception of water and cold alcohol. *Phthaliminoacetonediamylsulphone*,



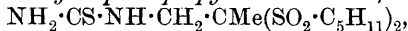
formed when the mercaptole is oxidised with potassium permanganate, crystallises from dilute alcohol in slender needles melting at 135° , and dissolves readily in chloroform, benzene, carbon tetrachloride, or acetone. When this substance is heated with strong potassium hydroxide solution, *potassium diamylsulphoneacetonephthalamate*, $\text{C}_{21}\text{H}_{32}\text{O}_7\text{NS}_2\text{K}$, is obtained in beautiful, white needles, which soften when heated, and melt at $151-152^\circ$; the free acid, $\text{CMe}(\text{SO}_2 \cdot \text{C}_5\text{H}_{11})_2 \cdot \text{CH}_2 \cdot \text{NH} \cdot \text{CO} \cdot \text{C}_6\text{H}_4 \cdot \text{CO}_2\text{H}$, is readily soluble in alcohol, ether, or chloroform, and melts indefinitely at $65-70^\circ$; the *ammonium*, *barium*, *lead*, *cadmium*, and *silver* salts were obtained.

Aminoacetonediamylsulphone, $\text{NH}_2 \cdot \text{CH}_2 \cdot \text{CMe}(\text{SO}_2 \cdot \text{C}_5\text{H}_{11})_2$, crystallises from dilute alcohol as a white mass consisting of slender needles, softens at 80° , melts at $104-106^\circ$, and dissolves readily in all the ordinary solvents excepting water. The *hydrochloride* forms slender, white needles, sinters at 77° , and melts at $85-88^\circ$; the *platinichloride*, $(\text{C}_{13}\text{H}_{29}\text{O}_4\text{NS}_2)_2 \cdot \text{H}_2\text{PtCl}_6$, crystallises from dilute hydrochloric acid in yellow needles, and melts and decomposes at $219-220^\circ$.

β -Diamylsulphonepropylcarbamide,

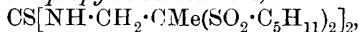


crystallises from dilute alcohol in microscopic needles melting at $215-216^\circ$. *β -Diamylsulphonepropylthiocarbamide*,



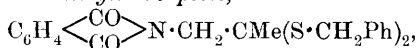
forms slender needles, sinters at 144° , and melts at $148-149^\circ$; it dissolves readily in most media, but is sparingly soluble in water and light petroleum.

Bis- β -diamylsulphonepropylthiocarbamide,



melts at $125-126^\circ$. *Phenyl- β -diamylsulphonepropylthiocarbamide*, $\text{NHPh} \cdot \text{CS} \cdot \text{NH} \cdot \text{CH}_2 \cdot \text{CMe}(\text{SO}_2 \cdot \text{C}_5\text{H}_{11})_2$, separates from dilute alcohol in slender needles and melts at 154° .

Phthaliminoacetonebenzylmercaptole,



separates from benzene in compact, opaque crystals melting at

137—138°. It is readily soluble in water or chloroform, and in hot benzene, alcohol, or carbon tetrachloride. *Phthaliminoacetonedibenzylsulphone*, $C_6H_4 \cdot C_2O_2 \cdot N \cdot CH_2 \cdot CMe(SO_2 \cdot CH_2Ph)_2$, crystallises from glacial acetic acid in slender needles melting at 244—245°, is sparingly soluble in most media, but somewhat readily soluble in hot glacial acetic acid, and readily in chloroform. When the sulphone is hydrolysed by hydrochloric acid, only a small quantity of a sulphur base is produced, and a complete breaking down appears to take place; if, however, it is heated for a short time with strong potassium hydroxide solution, and the liquid is then poured into water, a white precipitate is produced and a potassium salt remains in solution; the precipitate consists for the most part of unaltered sulphone, containing a small quantity of another substance, which may be separated by crystallisation from alcohol, and forms bundles of white crystals melting indefinitely at 85°. The filtrate from the insoluble matter, on addition of hydrochloric acid, gave a white, slimy precipitate and evolved sulphur dioxide. The precipitated acid, doubtless β -benzylsulphoneallylphthalamic acid, $CH_2Ph \cdot SO_2 \cdot CMe \cdot CH \cdot NH \cdot CO \cdot C_6H_4 \cdot CO_2H$, produced from the sulphone by elimination of benzenesulphonic acid (compare Autenrieth, Abstr., 1891, 203 and 204), crystallised from dilute alcohol in slender, white needles melting at 193—194°, and dissolved in hot water, alcohol, or acetic acid.

β -Benzylallylamine, $NH_2 \cdot CH_2 \cdot C(CH_2Ph) : CH_2$, is obtained by hydrolysing β -benzylsulphoneallylphthalamic acid with hydrochloric acid; it gives the isonitrile reaction, and decolorises a solution of bromine in chloroform; it has a basic odour and forms slender needles melting at 84—85°. The *hydrochloride* separates from absolute alcohol in glistening, felted needles melting at 195—200°. The *platinichloride*, $(C_{10}H_{13}N)_2 \cdot H_2PtCl_6$, forms granular crystals which darken at 200° and melt and decompose rapidly at 211—214°.

Phthaliminoacetonephenylmercaptole, $C_6H_4 \cdot C_2O_2 \cdot N \cdot CH_2 \cdot CMe(SPh)_2$, crystallises from benzene or dilute alcohol in slender, white needles melting at 164—165°, is readily soluble in most organic solvents, but sparingly so in water or light petroleum. *Phthaliminoacetonediphenylsulphone* crystallises from very dilute acetic acid in slender needles melting at 237—238°, is readily soluble in chloroform, hot acetic acid, or benzene, sparingly so in most other common media. When heated with strong hydrochloric acid at 180—190°, it yields a small quantity of *aminoacetonediphenylsulphone*, but is for the most part broken up into ethylenediphenylsulphone and phthalic acid; the *platinichloride* of the amino-base, $[NH_2 \cdot CH_2 \cdot CMe(SO_2Ph)]_2 \cdot H_2PtCl_6$, crystallises in orange-yellow needles, sinters at 135°, becomes transparent without liquefying at 150°, and decomposes at higher temperatures. A. L.

Cyclic Compounds. Behaviour of Cyclic Compounds at Low Temperatures. By WLADIMIR B. MARKOWNIKOFF (*Chem. Centr.*, 1899 ii, 19; from *J. Russ. Chem. Soc.*, 1899, 31, 356—358).—Naphthenes and their derivatives may be purified by fractional freezing, the melting point being an indication of the degree of purity. When hexanaphthene, prepared from naphtha, was cooled by means of

liquid carbon dioxide, it solidified at -46° , but after it had been separated three times by this means, it was found to solidify at -11° . Hexanaphtheneketone, $C_6H_{10}O$, solidifies at -45° and nitrohexanaphthene at -34° .
E. W. W.

Action of Zinc Methyl and Zinc Ethyl on Chlorohexanaphthene. By N. KURSANOFF (*Ber.*, 1899, 32, 2972—2974).—When chloronaphthene, $C_6H_{11}Cl$, is warmed with zinc methyl, some methane is evolved, small quantities only of unsaturated compounds are formed, and *methyl-naphthene* (*methylcyclohexane*), $C_6H_{11}Me$, is obtained in amount equal to 25 per cent. of the theoretical; this boils at $101-102^{\circ}$ under 752 mm. pressure, has the sp. gr. 0.7804 at $0^{\circ}/0^{\circ}$, 0.7641 at $20^{\circ}/0^{\circ}$, and is converted by bromine, in the presence of aluminium bromide, into pentabromotoluene, C_6MeBr_5 .

From chloro-(or iodo-)naphthene and zinc ethyl, ethane, ethylene, naphthylene, C_6H_{10} , and *ethyl-naphthene* (*ethylcyclohexane*), $C_6H_{11}Et$, are obtained, the last in 30 per cent. yield; also a mixture of paraffins, from which one, boiling at $242-243^{\circ}$ under 755 mm. pressure, was isolated. Ethylnaphthene boils at $132-133^{\circ}$ under 755 mm. pressure, and has the sp. gr. 0.7913 at $0^{\circ}/0^{\circ}$, 0.7772 at $20^{\circ}/0^{\circ}$.
C. F. B.

Action of Bromine on Chlorobenzenes in Presence of Aluminium Chloride. By A. MOUNEYRAT and CH. POURET (*Compt. rend.*, 1899, 129, 605—607).—The action of bromine on chloro-derivatives in presence of aluminium chloride seems to be a general method for the preparation of chlorobromo-derivatives of cyclic hydrocarbons, all the hydrogen being displaced. For example, chlorobenzene, *p*-dichlorobenzene, 1 : 2 : 4-trichlorobenzene, and 1 : 2 : 4 : 5-tetrachlorobenzene yield chlorobromo-derivatives which sublime readily in beautiful needles and have the following melting points; C_6Br_5Cl , $299-300^{\circ}$; $C_6Br_4Cl_2$ [$Cl_2 = 1 : 2$], $258-259^{\circ}$; [$Cl_2 = 1 : 4$], $278-278.5^{\circ}$; $C_6Br_3Cl_3$ [$Cl_3 = 1 : 2 : 4$], $260-261^{\circ}$; $C_6Br_2Cl_4$ [$Cl_4 = 1 : 2 : 4 : 5$], $246-246.5^{\circ}$.

With a suitable proportion of bromine, this reaction affords an easy method for the preparation of *p*-chlorobromobenzene from chlorobenzene.
C. H. B.

Electrolytic Modification of Sandmeyer's and Gattermann's Reactions. By EMIL VOTOČEK and E. ZENÍŠEK (*Zeit. Elektrochem.*, 1899, 5, 485—486).—Aniline, 30 per cent. hydrochloric acid, and sodium nitrite are mixed in the usual way; crystallised cupric chloride is then added and the solution electrolysed, a spiral of thick copper wire being used as anode, and a cylinder of sheet copper as cathode. The current density was 2.1 ampères per sq. dm., and the E.M.F. 10 volts. When the current is passed, nitrogen is given off and an oil rises to the surface; the current is stopped when nitrogen ceases to be evolved. The yield of chlorobenzene was 64 per cent. of the theoretical amount. Some azobenzene and phenol are also formed. Bromobenzene, *p*-chloro- and *o*-chloro-toluene, and β -chloronaphthalene were made in a similar way, the yields being usually better than those obtained by the use of finely divided copper.
T. E.

Reduction of Nitrobenzene with Sodium. By JULIUS SCHMIDT (*Ber.*, 1899, 32, 2911—2919).—Contrary to the statement of Hofmann and Geyger, sodium acts on nitrobenzene in ethereal solution at the ordinary temperature; when such a mixture is allowed to remain for 2 or 3 months with occasional shaking, it is found that all the sodium disappears and that a mixture of sodium oxide and disodiumphenylhydroxylamine, $\text{NPhNa}\cdot\text{ONa}$ or $\text{O}\cdot\text{NPhNa}_2$, is produced. This result is obtained more rapidly by carrying out the action in boiling toluene; in both cases, excess of nitrobenzene must be employed, and it is found that 4 atoms of sodium act on one molecule of the nitro-compound (compare Löb, *Abstr.*, 1897, i, 463). Phenylhydroxylamine is obtained from the disodium compound by adding an ethereal suspension of this substance to cold normal hydrochloric acid. The mixture of disodiumphenylhydroxylamine and sodium oxide is extremely unstable, and when exposed to air in thick layers it ignites spontaneously with explosive violence. When air is passed through a well cooled ethereal suspension of the product, sodium *o*-nitrophenoxide is produced, the yield being 50 per cent. of the theoretical; when a dilute solution of chromic acid is employed as the oxidising agent, nitrosobenzene is obtained, the yield in this case being 70 per cent. Ferric chloride, mercuric chloride, bleaching powder, and nitrous acid also oxidise the disodium compound to nitrosobenzene, whilst iodine converts it into nitrosobenzene and nitrobenzene. G. T. M.

Action of Sodium on *p*-Nitrotoluene. By JULIUS SCHMIDT (*Ber.*, 1899, 32, 2919—2920. Compare preceding abstract).—When an ethereal solution of *p*-nitrotoluene is shaken up with sodium, *p*-azoxytoluene, *p*-azotoluene, and a dark brown, spontaneously inflammable sodium derivative are produced. When treated with hydrochloric acid, the sodium compound yields a red, amorphous substance, which is probably identical with the azoxydihydrostilbene, $\text{O} \begin{array}{c} \diagup \text{N} \cdot \text{C}_6\text{H}_4 \cdot \text{CH}_2 \\ \diagdown \text{N} \cdot \text{C}_6\text{H}_4 \cdot \text{CH}_2 \end{array}$, investigated by Bender and Schultz (*Abstr.*, 1887, 268). G. T. M.

Electrolytic Reduction of *m*-Nitrotoluene. By ALBERT ROHDE (*Zeit. Elektrochem.*, 1899, 5, 322—324).—*m*-Nitrotoluene is very readily reduced by the method described by Elbs and Kopp (*Abstr.*, 1899, i, 270). The yield of *m*-azotoluene is 91 per cent. of the theoretical amount. Further reduction gives *m*-hydrazotoluene; this could not be obtained in the crystalline state, but was practically pure, for when converted into *m*-dimethylbenzidine, traces only of *m*-azotoluene were left. T. E.

Phenylacetylene, its Salts, and Halogen Substitution Derivatives. By JOHN ULRIC NEF (*Annalen*, 1899, 308, 264—328. Compare *Abstr.*, 1898, i, 102).—Several methods of preparing phenylacetylene are known, but the most economical consists in heating ω -bromostyrene or crude α -chlorostyrene with caustic potash (3 mols.) and a small proportion of alcohol. During the operation, phenylvinyl ethyl ether, $\text{CHPh}\cdot\text{CH}\cdot\text{OEt}$, is produced; it boils at 115° under 24 mm. pressure, and is formed when phenylacetylene is heated with alcoholic potash.

α -Bromostyrene, $\text{CPhBr}\cdot\text{CH}_2$, prepared by passing dried hydrogen

bromide into a solution of phenylacetylene in glacial acetic acid, has a sp. gr. 1.38 at 21°, and boils at 86—87° under 14 mm. pressure; it is indifferent towards sodium suspended in ether, but alcoholic sodium ethoxide regenerates phenylacetylene.

ω -Bromostyrene, $\text{CPh}\cdot\text{CHBr}$, obtained when the dibromide of cinnamic acid is heated with a 10 per cent. solution of sodium carbonate, has a sp. gr. 1.39 at 24.8°, and boils at 108° and 122° under pressures of 20 mm. and 36 mm. respectively; sodium wire, suspended in an ethereal solution of ω -bromostyrene, rapidly converts it into the sodium derivative of phenylacetylene.

$\alpha\omega$ -Dibromostyrene, $\text{CBrPh}\cdot\text{CHBr}$, prepared from phenylacetylene and bromine in ice-cold chloroform, boils at 132—135° under 15 mm. pressure; zinc dust acts vigorously on an alcoholic solution, regenerating phenylacetylene.

The sodium derivative of phenylacetylene is a very active substance, resembling zinc ethyl in the readiness with which it becomes added to carbonyl compounds; it is produced by the action of sodium on an ethereal solution of the hydrocarbon.

Benzoylphenylacetylene, $\text{CPh}\cdot\text{C}\cdot\text{COPh}$, obtained on adding benzoyl chloride to the sodium derivative of phenylacetylene suspended in dried ether, crystallises from light petroleum in colourless plates melting at 49—50°, and boils at 190—200° under 15 mm. pressure; the *diiodide* melts at 148—150°. Concentrated sulphuric acid converts benzoylphenylacetylene into α -hydroxybenzylideneacetophenone, originally known as dibenzoylmethane (compare J. Wislicenus, this vol., i, 37). *Acetylphenylacetylene*, $\text{CPh}\cdot\text{C}\cdot\text{COMe}$, prepared from acetyl chloride and the sodium derivative of phenylacetylene, boils at 122—128° under 12 mm. pressure; concentrated sulphuric acid converts it into benzoylacetone, and ethereal iodine gives rise to the *diiodide*, which melts at 102°. Ethyl chlorocarbonate acts on the sodium derivative of phenylacetylene, forming ethyl propiolate.

Acetophenonephenylacetylene, $\text{CPh}\cdot\text{C}\cdot\text{CMePh}\cdot\text{OH}$, produced when acetophenone is added to ether in which the sodium derivative of phenylacetylene is suspended, crystallises from petroleum in colourless needles and melts at 77°, boiling at 190—198° under 18 mm. pressure. *Benzophenonephenylacetylene*, $\text{CPh}\cdot\text{C}\cdot\text{CPh}_2\cdot\text{OH}$, crystallises from a mixture of benzene and petroleum, and melts at 82°.

Dibenzoxystilbene (isobenzil), $\text{C}_2\text{Ph}_2(\text{OBz})_2$, prepared by the action of benzoyl chloride or benzoic anhydride on the sodium derivative of benzil, separates from ether in colourless, hemimorphic, monoclinic crystals [$a:b:c=0.9682:1.08049$; $\beta=100^\circ 34.5'$]. It melts at 159°. *Diacetoxystilbene*, $\text{C}_2\text{Ph}_2(\text{OAc})_2$, separates from ether in colourless, monoclinic crystals, and melts at 118° [$a:b:c=2.828:1.3242$; $\beta=93^\circ 4'$]. It appears to be identical with the β -acetyl derivative of stilbenediol, described by Thiele (Abstr., 1899, i, 609). *Benzoylbenzhydrol*, $\text{COPh}\cdot\text{CPh}_2\cdot\text{OH}$, obtained from benzil, bromobenzene, and sodium melts at 83°; alcoholic potash resolves it into benzhydrol and benzoic acid, and its production is analogous to the formation of triphenylcarbinol from carbon monoxide, bromobenzene, and sodium (Frey, Abstr., 1896, i, 99).

In view of the properties currently ascribed to iodophenylacetylene,

the author has expressed the opinion (*loc. cit.*) that the substance belongs to the acetylidene series; closer examination, however, has brought to light its true character as an acetylene derivative, $\text{CPh}:\text{Cl}$. It is most conveniently prepared by the action of iodine on the silver or sodium derivative of phenylacetylene, and forms a colourless oil having a sweet odour; it boils at 117° under 15 mm. pressure, and has a sp. gr. 1.75 at 23° . A mixture of concentrated sulphuric acid with glacial acetic acid converts it into iodoacetophenone. The compound $\text{C}_{12}\text{H}_9\text{O}_2\text{I}$, obtained by heating iodophenylacetylene with silver acetate and glacial acetic acid, boils at 170° under 20 mm. pressure; concentrated sulphuric acid converts it into iodoacetophenone. The mercury derivative of phenylacetylene, $\text{Hg}(\text{C}_2\text{Ph})_2$, produced on heating iodophenylacetylene with mercury, crystallises from petroleum in colourless leaflets and melts at 125° ; it is also formed on adding an alcoholic solution of phenylacetylene to an aqueous mixture of potassium iodide and mercuric chloride to which caustic soda has been added.

Iodophenylacetyleneaniline, $\text{CPh}:\text{C}:\text{IH}\cdot\text{NHPh}$, prepared from iodophenylacetylene and aniline, crystallises from petroleum in flat, colourless needles and melts at $44\text{--}46^\circ$; when treated in ethereal solution with iodine, triiodostyrene and aniline are produced, whilst acetic anhydride gives rise to acetanilide and iodophenylacetylene. Zinc dust in alcohol converts iodophenylacetyleneaniline into aniline and phenylacetylene; when the substance is heated with ether at 100° during 3 hours, phenylacetylene and *p*-iodoaniline are formed. The production of iodophenylacetyleneaniline in the manner indicated is probably the first instance of a halogen atom becoming tervalent by direct addition of an amine, and it explains the fact that iodic cyanogen and aniline yield hydrogen cyanide and *p*-iodoaniline.

When iodophenylacetylene and ethyl malonate (2 mols.) are heated with alcoholic sodium ethoxide (1 mol.), phenylacetylene and ethyl ethanetetra-carboxylate are produced; the former is the sole product on heating the iodo-compound with alcoholic sodium ethoxide, potash, or potassium cyanide. Ethyl malonate in presence of zinc dust appears to yield ethyl styrenemalonate, $\text{CHPh}:\text{CH}\cdot\text{CH}(\text{CO}_2\text{Et})_2$, and ethyl phenylacetylenemalonate, $\text{CPh}:\text{C}\cdot\text{CH}(\text{CO}_2\text{Et})_2$. Numerous unsuccessful attempts have been made to convert iodophenylacetylene into tetralkylammonium iodides, $\text{CPh}:\text{C}\cdot\text{NR}_3\text{I}$, by means of tertiary amines; experiments have also been carried on with iodoallylene, $\text{CMe}:\text{Cl}$, a colourless, non-toxic oil, which boils at $109\text{--}110^\circ$, has a sp. gr. 2.08 at 22° , and is devoid of the disagreeable odour of acetylidene compounds.

ω -Dibromostyrene, $\text{CHPh}:\text{CBr}_2$, prepared by the action of alcoholic potash on ω -bromostyrene dibromide, boils at $135\text{--}136^\circ$ under 17 mm. pressure, and has a sp. gr. 1.819 at 22° ; when the vapour is passed over heated copper, phenylacetylene is produced, but phenylacetylidene is not formed.

Bromophenylacetylene, $\text{CPh}:\text{CBr}$, obtained from ω -dibromostyrene or from phenylacetylene dibromide by means of alcoholic potash and by heating the silver dibromocinnamates, is a colourless, non-toxic oil having a sweet odour; it boils at 96° under 15 mm. pressure, and

has a sp. gr. 1.456 at 24.2°. Concentrated sulphuric acid converts it into bromoacetophenone, whilst sodium in ether gives rise to phenylacetylene; caustic potash dissolved in methyl or ethyl alcohol, and sodium ethoxide dissolved in alcohol, resolves bromophenylacetylene into phenylacetylene and phenylacetic acid. In general behaviour, bromophenylacetylene resembles the iodo-derivative; the *diiodide*, $\text{CPh}\cdot\text{CBrI}$, crystallises from petroleum in transparent, yellow plates, and melts at 65—66°.

Chlorophenylacetylene, $\text{CPh}\cdot\text{CCl}$, prepared from dichlorostyrene and alcoholic potash (compare Biltz, Abstr., 1897, i, 573), boils at 74° under 14 mm. pressure, and has a sweet, agreeable odour; *phenylchlorovinyl ethyl ether*, $\text{CHPh}\cdot\text{CCl}\cdot\text{OEt}$, is a bye-product boiling at 129—130° under 19 mm. pressure, and yields phenylacetic acid under the influence of alcoholic potash. When chlorophenylacetylene is heated with alcoholic potash at 110—130° during 5 hours, phenylacetic acid is produced along with an oil which boils at 142—145° under 12 mm. pressure, and probably consists of chlorophenylacetylene *dialcoholate*, $\text{CH}_2\text{Ph}\cdot\text{CCl}(\text{OEt})_2$; this is a fresh instance of the resemblance between the cyanohalogenes and the halogen derivatives of phenylacetylene.

Triethyl α -naphthol-2-carboxy-3-malonate, $\text{C}_6\text{H}_4 \begin{matrix} \text{C(OH)}\cdot\text{C}\cdot\text{CO}_2\text{Et} \\ \text{CH}=\text{C}\cdot\text{CH}(\text{CO}_2\text{Et})_2 \end{matrix}$, prepared by the action of alcoholic sodium ethoxide on chlorophenylacetylene and ethylic malonate, crystallises from alcohol in colourless needles and melts at 88—89°; ferric chloride develops a greenish-blue coloration, and phenyldiazonium chloride yields a yellow azo-derivative. Hydrolysis, followed by elimination of carbon dioxide, gives rise to 1:3-hydroxymethylnaphthalene.

Metallic copper and silver act on perbromoethylene at high temperatures, but the sole products are carbon and the metallic bromides; zinc dust and alcohol yield acetylene and bromoacetylidene. Fuming nitric acid oxidises perbromoethylene to tribromoacetic acid. Alcoholic potash converts dibromoethylene, $\text{CBr}_2\cdot\text{CH}_2$, into bromoacetylidene. Iodopropiolic acid and its salts are readily changed into diiodoacetylidene and acetylene, the odour of the former becoming perceptible when the acid is recrystallised or fused, and when aqueous solutions of the salts are heated at 60—90°. Silver iodopropiolate decomposes spontaneously at the ordinary temperature, yielding diiodoacetylidene, carbon dioxide, and the silver derivative of acetylene.

When bromine acts on an aqueous solution of iodopropiolic acid, 15 per cent. of the theoretical amount of carbon dioxide is produced, along with tribromoacrylic acid, the dibromide of iodopropiolic acid, tribromoiodoethylene, $\text{CBr}_2\cdot\text{CBrI}$, dibromodiiodoethylene, and tetrabromoethylene (compare Homolka and Stolz, Abstr., 1885, 1198).

M. O. F.

Naphtha Tar. By NICOLAI N. LJUBAVIN [with RESWJAKOFF, RUDENKO and AREFÉEFF] (*Chem. Centr.*, 1899, ii, 118; from *J. Russ. Chem. Soc.*, 1899, 31, 358—364).—The tar, which is obtained from the naphtha residues in the manufacture of illuminating gas, yields a fraction boiling at 235—245° which contains, not only benzene,

naphthalene, and anthracene, but also β -methylnaphthalene. From the fraction boiling at $240\text{--}250^\circ$, after removing the crystals formed on cooling, α -methylnaphthalene was isolated. The volatile acids and phenols are not present in sufficient quantity in the tar to allow of isolation. Organic bases were obtained from the fractions boiling between 215° and 256° (compare Ljetni, *J. Russ. Chem. Soc.*, 6, I, 274; 9, I, 269; 10, I, 237. *Dingl. Pol. J.*, 239, 72; Rudnéeff, *Dingl. Pol. J.*, 239, 72; Nikiforoff, *Chem. Zeit.*, 1896, 8).

E. W. W.

Conversion of 1:8- and 1:5-Dinitronaphthalenes into Nitro-nitrosonaphthols. By CARL GRAEBE (*Ber.*, 1899, 32, 2876—2880. Compare Friedländer, *Abstr.*, 1895, i, 543).—When the 1:8- and 1:5-dinitronaphthalenes are heated at $40\text{--}50^\circ$ with fuming sulphuric acid, they are converted into isomerides soluble in alkalis (*Chem. Centr.*, 1897, i, 728 and 1079). The compound derived from the 1:8-dinitronaphthalene is identified as being 8-nitro-1-nitroso-1-naphthol. On treatment with hot dilute nitric acid, it yields a trinitronaphthol identical with Kehrman's and Haberkant's naphthopiepic acid (*Abstr.*, 1899, i, 62); the latter substance must have one of the following constitutions [$(\text{NO}_2)_3:\text{OH} = 1:3:5:4$ or $1:3:8:4$], and it follows from the authors' experiments that the latter orientation is the correct one. A direct proof that the migrating oxygen atom of the 1:8-dinitronaphthalene enters the para-position relatively to the nitroso-group is furnished by the following data. The nitronitrosonaphthol is reduced with ammonium hydrosulphide to a diamino-naphthol, whilst with tin and hydrochloric acid it yields an aminodihydroxynaphthalene; the latter compound forms a triacetyl derivative melting at 165° ; this substance, on hydrolysis with potash, yields acetylaminodihydroxynaphthalene, and the monacetyl compound, when oxidised with dilute sulphuric acid and dichromate, is converted into 8-acetyl-amino-1:4-naphthaquinone. That this oxidation product is really a paraquinone is shown by the fact that it does not condense with *o*-phenylenediamine. The nitronitrosonaphthol obtained from the 1:5-dinitronaphthalene when warmed with dilute nitric acid yields a trinitronaphthol [$(\text{NO}_2)_3:\text{OH} = 1:3:5:4$], and is reduced by tin and hydrochloric acid to a diaminonaphthol. G. T. M.

Action of Benzenediazonium Chloride on Alkaline Solutions of Nitrosophenol. By WALTHER BORSCHKE (*Ber.*, 1899, 32, 2935—2940). The action of benzenediazonium chloride on alkaline solutions of nitrosophenol is a very complicated one, and five products have hitherto been isolated; amongst these are two phenolic substances which are precipitated by passing carbon dioxide into the alkaline solution.

Nitrosohydroxydiphenyl, $\text{NO}\cdot\text{C}_{12}\text{H}_8\cdot\text{OH}$ [$\text{OH}:\text{NO} = 2:5$], the more soluble of these two compounds crystallises from alcohol in yellow scales and melts at 174° ; it readily dissolves in solutions of the caustic alkalis, giving yellowish-red solutions, and is appreciably soluble in concentrated solutions of sodium carbonate and sodium hydrogen carbonate; it gives the Liebermann nitroso-reaction. The *benzoyl*

derivative crystallises in brownish-yellow leaflets, and decomposes at $173-174^{\circ}$.

Aminohydroxydiphenyl hydrochloride, prepared by reducing the nitroso-compound with tin and hydrochloric acid, forms colourless crystals melting at 214° ; the *base* is obtained in the form of unstable, colourless needles; it melts at 192° .

Diphenylquinone, $C_6H_5PhO_2$, obtained by oxidising the preceding base with potassium dichromate and dilute sulphuric acid, crystallises in lustrous, brown needles and melts at 107° . By the action of reducing agents, the quinone yields a very soluble *quinol* and an intermediate *compound*, crystallising from dilute acetic acid in dark violet, glistening leaflets and melting at $176-177^{\circ}$. A *dinitro*-compound is produced by treating nitrosohydroxydiphenyl with nitric acid; it crystallises in flattened needles or rhombic prisms, and melts at $203-204^{\circ}$.

Nitrosohydroxydiphenylbenzene, $NO \cdot C_6H_5Ph_2 \cdot OH$ [$\{Ph_2 : OH : NO = 1 : 3 : 2 : 5\}$], the second phenolic compound, is more readily precipitated by carbon dioxide than nitrosohydroxydiphenyl; it crystallises from acetic acid in olive-green leaflets and melts at $242-244^{\circ}$; it gives the Liebermann reaction, and yields a *benzoyl* derivative melting at $163-164^{\circ}$.

Aminohydroxydiphenylbenzene hydrochloride, produced by reducing the preceding nitroso-compound with tin and hydrochloric acid, crystallises in colourless, silky needles, and melts at 240° ; the *base* crystallises from alcohol in colourless, nacreous leaflets melting at $146-147^{\circ}$, these turn red on exposure to light and air.

Diphenylbenzoquinone, $C_6H_5Ph_2O_2$, obtained by oxidising the preceding base, crystallises from dilute acetic acid in long, red needles, and melts at $137-138^{\circ}$; the *quinol* crystallises in colourless leaflets and melts at $177-178^{\circ}$.

The exact constitution of the two nitroso-compounds has not been ascertained with certainty, but it seems probable that the phenyl radicles enter the ortho-positions relatively to the hydroxyl group.

G. T. M.

Action of Bromine on *m*-Chloro-, *m*-Bromo-, and *m*-Iodoanilines. II. By HENRY L. WHEELER and WILLIAM VALENTINE (*Amer. Chem. J.*, 1899, **22**, 266—280).—When bromine vapour (1 mol.) is led into a solution of *m*-chloroaniline in glacial acetic acid, the principal products are 3-chloro-4-bromoaniline and 3-chloro-4 : 6-dibromoaniline, the former predominating, whilst a small quantity only of 3-chloro-2 : 4 : 6-tribromoaniline is formed. *3-Chloro-4-bromoaniline* crystallises from dilute alcohol in colourless plates, melts at $67-68^{\circ}$, and on eliminating the amino-group yields *o*-chlorobromobenzene (Dobbie and Marsden, *Trans.*, 1898, **73**, 255); the *hydrochloride* crystallises in colourless needles, and, when heated, blackens at 210° ; the *sulphate* forms colourless plates, whilst the *picrate* crystallises in yellow needles and melts at 141° . *3-Chloro-4-bromoacetanilide*, obtained almost quantitatively on adding bromine (1 mol.) to *m*-chloroacetanilide dissolved in glacial acetic acid, melts at 125° , and, when dissolved in cold nitric acid of sp. gr. 1.52, yields 3 : 4 : 6-chlorobromo-

nitroacetanilide, $\text{NO}_2 \cdot \text{C}_6\text{H}_4\text{ClBr} \cdot \text{NHAc}$, which crystallises from absolute alcohol in colourless plates and melts at $129-130^\circ$; 3:4:6-*chlorobromonitroaniline*, obtained from the latter, crystallises from alcohol in long, yellow needles, melts at $202-203^\circ$, and yields 4-*chloro-3-bromonitrobenzene* when treated with nitrous acid in alcohol. This separates from alcohol in light-yellow needles, melts at 60° , and, on reduction, yields 4-*chloro-3-bromoaniline*, which crystallises in colourless plates and melts at 78° ; the same base is also formed on reducing the product* obtained by dissolving *o*-chlorobromobenzene in fuming nitric acid, which hence probably consists largely of 4-*chloro-3-bromonitrobenzene*. 3-*Chloro-4-bromo-2:6-dinitroaniline*, obtained by the action of nitric acid on 3-*chloro-4-bromoaniline* at 100° , crystallises from absolute alcohol in dark yellow prisms and melts at $169-170^\circ$. 3-*Chloro-4:6-dibromoaniline* crystallises from alcohol in thin, colourless plates and melts at $79-80^\circ$.

The action of bromine vapour (1 mol.) on *m*-bromoaniline dissolved in glacial acetic acid yields principally 3:4-dibromoaniline together with a mixture of 3:4:6-*tribromoaniline*, and, in smaller proportion, 2:3:4-*tribromoaniline*, whilst traces of 2:3:4:6-*tetrabromoaniline* are also formed. 3:4-Dibromoaniline yields a *picrate*, $\text{C}_6\text{H}_5\text{NBr}_2 \cdot \text{C}_6\text{H}_3\text{N}_3\text{O}_7$, which crystallises from water in yellow needles and melts at 149° ; the *hydrochloride* crystallises from dilute hydrochloric acid in colourless prisms and decomposes at $220-230^\circ$, whilst the *sulphate* forms colourless plates. 3:4:6-*Tribromoaniline* melts at $85-86^\circ$ and yields 1:3:4-*tribromobenzene* on eliminating the amino-group; 3:4:6-*tribromoacetanilide*, $\text{C}_8\text{H}_6\text{NOBr}_3$, prepared from it, or by the action of bromine (1 mol.) on 3:6-dibromoacetanilide (*infra*) dissolved in glacial acetic acid, crystallises from alcohol in colourless needles and melts at $188-189^\circ$. 3:6-*Dibromoacetanilide*, $\text{C}_6\text{H}_4\text{Br}_2 \cdot \text{NHAc}$, prepared by acetylating 3:6-dibromoaniline (Meyer and Stüber, *Annalen*, 165, 180), melts at $171-172^\circ$. 2:3:4-*Tribromoaniline* was not isolated, but its presence in the fraction from which 3:4:6-*tribromoaniline* is obtained is proved by the formation of 1:2:3-*tribromobenzene* on treating this fraction with nitrous acid in alcohol.

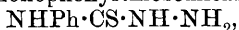
The principal product of the action of bromine (1 mol.) on *m*-iodoaniline is 4:6-dibromo-3-iodoaniline; a slightly smaller amount of 4-bromo-3-iodoaniline is also formed, together with traces of 2:4:6-*tribromo-3-iodoaniline*. 4-*Bromo-3-iodoaniline* crystallises from alcohol in colourless plates, melts at 77° , and is also obtained by reducing 4-*bromo-3-iodonitrobenzene* melting at $95-96^\circ$, prepared from 6-bromo-3-nitroaniline; the *hydrochloride* crystallises from alcohol in long, slender, colourless needles, and, when heated, decomposes at about 210° ; the *sulphate* crystallises from dilute sulphuric acid in colourless plates, whilst the *picrate*, $\text{C}_6\text{H}_5\text{NBrI} \cdot \text{C}_6\text{H}_3\text{N}_3\text{O}_7$, separates from water in yellow needles and melts at $158-159^\circ$. 4-*Bromo-3-iodoacetanilide*, prepared from the base, crystallises from alcohol and melts at

* This nitration-product, the melting point of which, after several crystallisations, remains constant at $49-50^\circ$, probably consists of an isomorphous mixture of 3-bromo-4-chloro- and 3-chloro-4-bromo-nitrobenzene.—W. A. D.

138—139°. 4 : 6-Dibromo-3-iodoaniline forms long, colourless prisms, and melts at 81°, whilst 2 : 4 : 6-tribromo-3-iodoaniline crystallises from alcohol in minute, colourless prisms or plates, and melts at 115—116°. W. A. D.

Formation of Phenylcarbylamine by the Electrolysis of Alkaline Alcoholic Solutions of Nitrobenzene and Aniline. By JOHANN MÖLLER (*Zeit. Elektrochem.*, 1899, 5, 463—464).—A solution of nitrobenzene, caustic soda, and water in alcohol was electrolysed at 60—70° for 36 hours with a current density of 9 to 10 ampères per sq. dm. Platinum electrodes and no diaphragm were used. A strong smell of phenylcarbylamine was noticed, but the substance was not isolated. The characteristic carbylamine odour is also noticed when alkaline solutions of aniline, or of *o*-nitro- or *p*-nitro-toluene, are electrolysed. T. E.

Action of Hydrazine on Thiocarbanilide. By MAX BUSCH (*Ber.*, 1899, 32, 2815—2818).—Hydrazine hydrate interacts with thiocarbanilide to form varying proportions, according to the conditions, of aniline and monophenylthiosemicarbazide,



together with an *acid* containing sulphur which crystallises in prisms and melts at 205°, a *base*, $\text{C}_{19}\text{H}_{21}\text{N}_5$, melting at 105°, and a neutral *substance* free from sulphur which melts at 232°. The *base*, $\text{C}_{19}\text{H}_{21}\text{N}_5$, is formed almost exclusively on heating the thiocarbanilide with an excess of hydrazine hydrate and alcoholic potash for 4—5 hours at 110°, and crystallises from ether in stout, transparent needles; when heated at 180°, it loses aniline and is partially converted into the neutral substance melting at 232°; the *hydrochloride* of the base is crystalline, but rapidly decomposes, the *oxalate*, $\text{C}_{19}\text{H}_{21}\text{N}_5 \cdot \text{C}_2\text{H}_2\text{O}_4$, crystallises from ether in colourless prisms and melts at 160°, whilst the *picrate*, $\text{C}_{19}\text{H}_{21}\text{N}_5 \cdot \text{C}_6\text{H}_3\text{N}_3\text{O}_7$, forms small, yellow prisms and melts at 135°. The base behaves towards aldehydes as a primary amine; the benzylidene compound could not be obtained crystalline, but the *m*-nitrobenzylidene derivative, $\text{C}_{19}\text{H}_{19}\text{N}_5 \cdot \text{CH} \cdot \text{C}_6\text{H}_4 \cdot \text{NO}_2$, separates from alcohol in canary-yellow crystals and melts at 130°. Under the influence of nitrous acid, aniline is split off from the base, and the same holds true with benzoyl chloride, benzoylaniline being formed; the base thus appears to be *trianilinomethylhydrazine*, $\text{C}(\text{NHPh})_3 \cdot \text{NH} \cdot \text{NH}_2$, formed by the thiocarbanilide initially undergoing resolution, under the influence of the alkali, partly into aniline, partly into carbodiphenylimide, the latter subsequently combining with hydrazine and aniline. The author intends subjecting this view to the test of experiment.

Di-*p*-chlorothiocarbanilide, under the conditions given above, does not behave like thiocarbanilide, but yields an *amino-p-chlorophenyl-guanidine*, $\text{C}(\text{NH} \cdot \text{C}_6\text{H}_4\text{Cl})_2 \cdot \text{NH} \cdot \text{NH}_2$, melting at 135°, together with a small quantity of di-*p*-chlorocarbanilide, $\text{CO}(\text{NH} \cdot \text{C}_6\text{H}_4\text{Cl})_2$. W. A. D.

Chemical Composition of Norwegian Tar from Conifers. By KNUT STRÖM (*Arch. Pharm.*, 1899, **237**, 525—543).—This tar is made in the following primitive fashion. Roots of the Scotch fir (*Pinus sylvestris*) are chopped up, packed in a pit or a crevice of the rocks, and then set on fire. When the whole is well alight, turf or earth is piled over it so that but very little air can find access; at the close of the operation, the tar is ladled out from the bottom of the pit or crevice.

The tar contains volatile acids, 4·8 (calculated as acetic; nearly 9/10 were formic and acetic); phenols, 11; hydrocarbons, 61 per cent. (of these about 1/7 solid, the rest liquid). Formic, acetic, propionic, normal butyric, valeric (normal and also Renard's acid, *Ann. Chim. Phys.*, [vi], 1, 253), α -methylvaleric, normal hexoic, cœnanthylic, and normal octoic acids were detected, and it is probable that pelargonic, decolic, and inactive pimic acids were also present. Of the phenols, cresol, guaiacol, creosol, ethylguaiacol, propylguaiacol, and two others of the composition $C_{11}H_{16}O_2$ (b. p. 260—265°) and $C_{12}H_{14}O_2$ (b. p. 300°) respectively, were detected. Amongst the hydrocarbons were terpenes and retene. The acids were separated by fractional distillation; the phenols, in the same way, combined with crystallisation of their picrates; the hydrocarbons, by distillation, combined with crystallisation of such fractions as solidified. C. F. B.

Chloroanisidines and *m*-Chloroanisole. By FRÉDÉRIC REVERDIN and F. ECKHARD (*Ber.*, 1899, **32**, 2622—2627).—It has been shown that a migration of the halogen atom occurs when *p*-iodoanisole, *p*-iodophenetole, *p*-bromoanisole, and *p*-bromophenetole are nitrated (Abstr., 1896, i, 475; 1897, i, 27; 1898, i, 180; and 1899, i, 266); no change of this kind takes place, however, during the nitration of *o*-chloroanisole and its para-isomeride. The former substance yields *o*-chloro-*p*-nitroanisole (OMe:Cl:NO₂ = 1 : 2 : 4), whilst *p*-chloro-*o*-nitroanisole and a small quantity of dinitro-*p*-chlorophenol are obtained from the para-compound.

o-Chloro-*p*-anisidine (OMe:Cl:NH₂ = 1 : 2 : 4), obtained by reducing the corresponding nitro-compound with tin and hydrochloric acid, crystallises from petroleum in small, white needles melting at 62°; it is not volatile in steam. The *acetyl* derivative crystallises from water in white needles and melts at 94°; the *picrate* crystallises from dilute alcohol in yellow needles melting and decomposing at 186°.

p-Chloro-*o*-anisidine (OMe:Cl:NH₂ = 1 : 4 : 2) is soluble in the ordinary organic solvents, and crystallises in white needles melting at 82°; it is volatile in steam. The *acetyl* derivative crystallises in white needles and melts at 104°; the *picrate* forms pale yellow needles decomposing at 194°.

By reducing *m*-nitroacetyl-*o*-anisidine (OMe:NHAc:NO₂ = 1 : 2 : 5) with iron and acetic acid, an acetyl-diamine is produced, which is converted by the Sandmeyer reaction into *m*-chloro-*o*-anisidine; this compound is identical with the base melting at 52° obtained by Herold (Abstr., 1882, 1287) as a bye-product in the reduction of *o*-nitroanisole with tin and hydrochloric acid.

m-Chloroanisole, produced by eliminating the amino-group from the

preceding base, is obtained as a pale yellow oil; it boils at 191—192° under 728 mm. pressure, the boiling points of the ortho- and para-isomerides under this pressure being 197—198° and 193—194° respectively. The meta-compound is also prepared by substituting hydrogen for the amino-group of *m*-nitro-*o*-anisidine, reducing the nitroanisole, and finally replacing the amino-group in the resulting amine by chlorine. *m*-Chloroanisole yields a *nitro*-derivative melting at 58°.

o-Chloro-*m*-nitroanisole (OMe:Cl:NO₂ = 1 : 2 : 5) is obtained by replacing the amino-group of *m*-nitro-*o*-anisidine by chlorine; it crystallises from petroleum in yellowish-white needles melting at 83°.

o-Chloro-*m*-anisidine (OMe:Cl:NH₂ = 1 : 2 : 5), obtained by reducing the preceding nitro-compound, crystallises from benzene and petroleum in white needles, and melts at 77°; the *acetyl* derivative crystallises in white needles and melts at 122°. The azo- β -naphthol compounds of *m*-chloro-*o*-anisidine and *p*-chloro-*o*-anisidine, when developed on cotton fibre, have a brownish-violet colour resembling that of the corresponding azo-derivative of anisidine.

G. T. M.

Phenacetin. By GEORG COHN (*Annalen*, 1899, 309, 233—238).—When phenacetin is heated with concentrated sulphuric acid, phenacetinsulphonic acid, SO₃H·C₆H₅(OEt)·NHAc, is produced; the *sodium* salt crystallises from dilute alcohol in minute, white needles, and is insoluble in absolute alcohol. If 80—90 per cent. sulphuric acid is employed, ethyl acetate is eliminated from phenacetin, *p*-aminophenolsulphonic acid and *p*-aminophenol being produced. Fifty per cent. sulphuric acid converts phenacetin into the sulphate, and if the acid is boiled, acetic acid and phenetidine are produced.

Sulphonic acids have been prepared also from benzoylphenetidine, lactophenin, *p*-ethoxyphenylurethane, *p*-phenetylcarbamide, and diacetylaminophenol.

M. O. F.

Transformation of Hydroxamic Acids. By JOHANNES THIELE and ROBERT HOWSON PICKARD (*Annalen*, 1899, 309, 189—205. Compare Thiele and Schleussner, *Abstr.*, 1897, i, 380).—The *potassium* derivative of acetylbenzhydroxamic acid crystallises in leaflets, and yields diphenylcarbamide when the aqueous solution is warmed, phenylcarbamide being obtained by the action of ammonia on dibenzhydroxamic acid and acetylbenzhydroxamic acid. An alcoholic solution of potassium dibenzhydroxamate yields diphenylcarbamide when boiled with aniline, and α -phenyl- β -phenylethylcarbamide with ethylaniline; ethylamine converts it into phenylethylcarbamide. The hydrazide of phenylcarbamic acid is produced when potassium dibenzhydroxamate is heated with hydrazine, and phenylurethane is formed on boiling an alcoholic solution of potassium acetylbenzhydroxamate or dibenzhydroxamate, methyl phenylcarbamate being formed when methyl alcohol is used.

Cinnamhydroxamic acid, prepared from ethyl cinnamate, hydroxylamine, and sodium ethoxide, crystallises from chloroform and melts at 111.5°. *Acetylcinnamhydroxamic acid*, CHPh:CH·C(OH):N·OAc, obtained by the action of acetic anhydride, crystallises from benzene in colourless, lustrous plates, and melts at 112°; the *potassium*

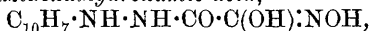
derivative decomposes in moist air. *Benzoylcinnamhydroxamic acid*, $\text{CHPh}\cdot\text{CH}\cdot\text{C}(\text{OH})\cdot\text{N}\cdot\text{OBz}$, prepared from cinnamhydroxamic acid and benzoyl chloride, crystallises from alcohol in long needles and melts at 144° ; the *potassium* derivative is crystalline. Amines do not convert the acylcinnamhydroxamic acids into the corresponding carbamides; Ammonia regenerates cinnamhydroxamic acid, and aniline gives rise to cinnamanilide. Boiling ethyl alcohol produces *ethyl styrylcarbamate*, $\text{CHPh}\cdot\text{CH}\cdot\text{NH}\cdot\text{CO}_2\text{Et}$, melting at 89° , and methyl alcohol generates *methyl styrylcarbamate*, which melts at 115° ; when these salts are hydrolysed with alcoholic potash, phenylacetaldehyde is formed.

Dihydrocinnamhydroxamic acid, $\text{CH}_2\text{Ph}\cdot\text{CH}_2\cdot\text{C}(\text{OH})\cdot\text{NOH}$, obtained by heating ethyl dihydrocinnamate with alcoholic hydroxylamine and sodium ethoxide at $45\text{--}50^\circ$ during four hours, crystallises from benzene in long, colourless needles and melts at 78° ; the *copper* derivative is insoluble in water. *Acetyldihydrocinnamhydroxamic acid*, $\text{CH}_2\text{Ph}\cdot\text{CH}_2\cdot\text{C}(\text{OH})\cdot\text{N}\cdot\text{OAc}$, crystallises from water in lustrous plates and melts at 99° ; the *potassium* and *ammonium* derivatives are crystalline. *Benzoyldihydrocinnamhydroxamic acid*, $\text{CH}_2\text{Ph}\cdot\text{CH}_2\cdot\text{C}(\text{OH})\cdot\text{N}\cdot\text{OBz}$, crystallises from alcohol in long, lustrous needles and melts at 117° .

Symmetrical diphenethylcarbamide, $\text{CO}(\text{NH}\cdot\text{CH}_2\cdot\text{CH}_2\text{Ph})_2$, prepared from the acylcinnamhydroxamic acids by warming aqueous solutions of the alkali derivatives, crystallises from dilute alcohol in large plates and melts at 137° ; hydrochloric acid at 180° resolves it into phenethylamine.

Phenylacetylhydroxamic acid, $\text{CH}_2\text{Ph}\cdot\text{C}(\text{OH})\cdot\text{NOH}$, produced when ethyl phenylacetate is heated with alcoholic hydroxylamine and sodium ethoxide, melts at 121° ; the *copper* derivative is insoluble in water. *Acetylphenylacetylhydroxamic acid*, $\text{CH}_2\text{Ph}\cdot\text{C}(\text{OH})\cdot\text{N}\cdot\text{OAc}$, also melts at 121° , and forms a crystalline *potassium* derivative; when an aqueous solution of the latter is warmed, symmetrical dibenzylcarbamide is produced, whilst aniline converts it into symmetrical phenylbenzylcarbamide.

α -Naphthylhydrazidoxalhydroxamic acid,

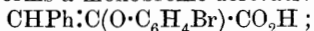


obtained from ethyl oxalate β -naphthylhydrazide (Freund, Abstr., 1892, 509), hydroxylamine, and sodium ethoxide, separates from alcohol in yellowish crystals, and melts at 184.5° , when it decomposes; the *triacetyl* derivative melts and decomposes at 155° . *β -Naphthylhydrazidoxalhydroxamic acid* melts and decomposes at 167° .

M. O. F.

Phenoxyacetic Acid. Bromination of Phenoxyacetic Acid. By ALB. J. J. VANDEVELDE (*Chem. Centr.*, 1899, ii, 91—92; from *Bull. Acad. roy. Belg.*, 1899, 204—211. Compare Abstr., 1899, i, 209).—Phenoxyacetophenone, $\text{OPh}\cdot\text{CH}_2\cdot\text{COPh}$, obtained by the action of phenoxyacetyl chloride on benzene or of sodium phenoxide on ω -chloroacetophenone, is a syrupy liquid and boils at $255\text{--}257^\circ$. Ethyl phenoxyacetic acid, $\text{CHPh}\cdot\text{C}(\text{OPh})\cdot\text{CO}_2\text{Et}$, prepared by means of ethylsulphuric acid, is a syrupy liquid, boils at $220\text{--}223^\circ$, and is

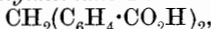
insoluble in water. The action of bromine on this compound gave no results, but the acid forms a monobromo-derivative,



this substance crystallises from benzene, melts at 191° , and is identical with *p*-bromophenoxyacetic acid, obtained by heating sodium *p*-bromophenoxyacetate with benzaldehyde in presence of acetic anhydride.

E. W. W.

Diphenylmethane-2:4'-dicarboxylic Acid. By HEINRICH LIMP-
RICHT [and THEODOR LACH] (*Annalen*, 1899, 309, 115—125. Compare following abstract).—*Diphenylmethane-2:4'-carboxylic acid*,



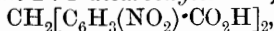
prepared by reducing benzophenone-2:4'-dicarboxylic acid with zinc dust and concentrated ammonia, contains $1\text{H}_2\text{O}$, and melts at 220° ; the *ammonium* salt melts at 214° , and yields diphenylmethane on distillation. The *barium* salt contains $3\text{H}_2\text{O}$, the *silver* salt is amorphous, and the *methylic* ester crystallises in white needles melting at 48° . The mixed *acetic anhydride*, $\text{CH}_2(\text{C}_6\text{H}_4\cdot\text{CO}\cdot\text{OAc})_2$, melts at 135° , and loses acetic anhydride at 140° , but this substance is not completely removed until the temperature reaches 280° , when *diphenylmethane-2:4'-dicarboxylic anhydride*, melting at 195° , sublimes in white needles. The *chloride* melts at 180° , and the *amide* forms long, silky needles melting at 236° ; the *dianilide* melts at 227° , and, when boiled, yields aniline and the *anil*, which crystallises from alcohol in yellow needles and melts at 218° .

Diphenylmethane diphenyl diketone, $\text{CH}_2(\text{C}_6\text{H}_4\cdot\text{COPh})_2$, prepared by heating the chloride of diphenylmethanedicarboxylic acid with benzene and aluminium chloride, melts at 234° ; *diphenylmethane ditolyl diketone* crystallises from glacial acetic acid in yellow needles, and melts at 162° .

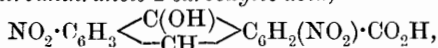
9-Anthranol-2-carboxylic acid, $\text{C}_6\text{H}_4\left\langle\begin{smallmatrix}\text{C}(\text{OH})\\ \text{CH}\end{smallmatrix}\right\rangle\text{C}_6\text{H}_3\cdot\text{CO}_2\text{H}$, obtained by dissolving diphenylmethanedicarboxylic acid in concentrated sulphuric acid, melts at $305\text{--}310^\circ$; reduction with zinc dust and ammonia converts it into *dihydroanthracene-2-carboxylic acid*, $\text{C}_6\text{H}_4\left\langle\begin{smallmatrix}\text{CH}_2\\ \text{CH}_2\end{smallmatrix}\right\rangle\text{C}_6\text{H}_3\cdot\text{CO}_2\text{H}$, which melts at 276° , and forms solutions exhibiting blue fluorescence.

Anthraquinone-2-carboxylic acid, $\text{C}_6\text{H}_4\left\langle\begin{smallmatrix}\text{CO}\\ \text{CO}\end{smallmatrix}\right\rangle\text{C}_6\text{H}_3\cdot\text{CO}_2\text{H}$, derived from anthranol-2-carboxylic acid by oxidation with potassium permanganate, crystallises from alcohol in yellow needles and melts at 281° .

Dinitrodiphenylmethane-2:4'-dicarboxylic acid,



prepared by dissolving diphenylmethanedicarboxylic acid in fuming nitric acid, melts at 215° , and when treated with concentrated sulphuric acid yields *dinitroanthranole-2-carboxylic acid*,



which crystallises from alcohol in reddish-yellow, transparent plates,

melts at 206°, and when oxidised with chromic acid is converted into *dinitroanthraquinone-2-carboxylic acid* melting at 315°.

Diaminodiphenylmethane-2:4'-dicarboxylic acid,



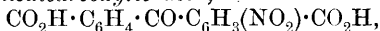
obtained by reducing the dinitro-acid with stannous chloride, melts at 265°; the *hydrochloride* forms white plates melting at 292°, and the *sulphate* crystallises in needles. *Dihydroxydiphenylmethane-2:4'-dicarboxylic acid*, $\text{CH}_2[\text{C}_6\text{H}_3(\text{OH})\cdot\text{CO}_2\text{H}]_2$, formed when nitrous acid acts on the diamino-acid, crystallises from alcohol in white needles and melts at 236°; the *barium* salt contains $1\text{H}_2\text{O}$. M. O. F.

Benzophenone-2:4'-dicarboxylic Acid. By HEINRICH LIMP-
RICHT (*Annalen*, 1899, 309, 96—114. Compare Abstr., 1895, i, 422).—Benzophenone-2:4'-dicarboxylic acid, $\text{CO}(\text{C}_6\text{H}_4\cdot\text{CO}_2\text{H})_2$, melts at 235°. The *ammonium* salt contains $2\text{H}_2\text{O}$, which is removed at 115°, and the anhydrous substance melts and decomposes at 190—195°; the *barium* salt contains $2\frac{1}{2}\text{H}_2\text{O}$, and the *silver* salt is anhydrous. The *chloride* crystallises from benzene or ether in monoclinic prisms, and melts at 102°; when treated with phosphorus pentachloride at 150° during several days, it yields the *tetrachloride*, which separates from benzene in yellow needles, and melts at 198°. The mixed *acetic anhydride*, $\text{CO}(\text{C}_6\text{H}_4\cdot\text{CO}\cdot\text{OAc})_2$, prepared by the action of boiling acetic anhydride, crystallises from glacial acetic acid and melts at 177°; when heated at 180—190°, it yields *benzophenone-2:4'-dicarboxylic anhydride*, which is also produced on distilling the acid, and crystallises from ether in aggregates of yellow needles melting at 184°. The *amide* melts at 285°, and the *imide* at 251°, and forms a crystalline *barium* derivative; the *anilide* crystallises in needles, melts at 210°, and yields *barium* and *silver* derivatives. The *dianilide* melts at 227°. The

4-isoxazolone, $\text{CO}\cdot\text{C}_6\text{H}_4\cdot\text{O}\text{---}\text{N}\text{---}\text{C}\cdot\text{C}_6\text{H}_4\cdot\text{CO}_2\text{H}$, prepared by heating an alcoholic solution of benzophenonedicarboxylic acid with hydroxylamine hydrochloride, crystallises in long needles and melts at 300°; the chloride of the acid yields, with hydroxylamine hydrochloride, the *dioxime* of the anhydride, $\text{C}_{15}\text{H}_{10}\text{O}_4\text{N}_2$, which melts at 213°. The *oxime* of the methyl salt melts at 190°, and the *phenylhydrazide* of the acid crystallises in white needles melting at 253°.

Benzophenone diethyl diketone, $\text{CO}(\text{C}_6\text{H}_4\cdot\text{COEt})_2$, prepared from benzophenonedicarboxylic chloride and zinc ethyl, crystallises from alcohol and melts at 105°. *Benzophenone diphenyl diketone*, $\text{CO}(\text{C}_6\text{H}_4\cdot\text{COPh})_2$, obtained when the chloride is heated gently with benzene and aluminium chloride, melts at 162°, and *benzophenone ditolyl diketone* gradually softens before fusion. *Benzophenonediphenyldiketonedicarboxylic acid*, $\text{CO}(\text{C}_6\text{H}_4\cdot\text{CO}\cdot\text{C}_6\text{H}_4\cdot\text{CO}_2\text{H})_2$, contains $\frac{1}{2}\text{H}_2\text{O}$, and melts at 185—190°; the *barium* salt is a white, crystalline powder.

Nitrobenzophenonedicarboxylic acid,



prepared by oxidising nitro-*p*-toluoyl-*o*-benzoic acid (Abstr., 1898, i, 322), crystallises from water in aggregates of minute, colourless needles, and melts at 230°; the *silver* salt blackens in light. M. O. F.

Mixed Methenyl Compounds. I. and II. Action of Ethyl Ethoxymethyleneacetoacetate and Ethoxymethylenemalonate on Ethyl Acetonedicarboxylate. By GIORGIO ERRERA (*Ber.*, 1899, 32, 2776—2792, 2792—2798. Compare Claisen, *Abstr.*, 1897, i, 592).—A 72 per cent. yield of *triethyl 4-hydroxy-2-methyltrimesate*, $\text{OH}\cdot\text{C}_6\text{HMe}(\text{CO}_2\text{Et})_3$, is obtained when an alcoholic solution of ethyl ethoxymethyleneacetoacetate is added to an alcoholic solution of the sodium derivative of ethyl acetonedicarboxylate; it separates from light petroleum in large, non-transparent, somewhat irregular, monoclinic crystals [$a:b:c = 1.003291 : 1 : 0.71533$; $\beta = 78^\circ 22' 13''$]; it melts at 47° and dissolves readily in most organic solvents, but is insoluble in water, and its alcoholic solution gives a reddish-violet colour with ferric chloride. Its *sodium* derivative is sparingly soluble in cold alcohol, and crystallises in colourless, felted needles, which are rapidly decomposed by boiling water, yielding the *sodium diethyl salt*. *Diethyl hydroxymethyltrimesate*, $\text{OH}\cdot\text{C}_6\text{HMe}(\text{CO}_2\text{H})(\text{CO}_2\text{Et})_2$, crystallises from a mixture of benzene and light petroleum in colourless, monoclinic needles [$a:b:c = 1.40879 : 1 : 0.80810$; $\beta = 85^\circ 6' 52''$]; it melts at $137\text{—}138^\circ$ and is readily soluble in most solvents, its alcoholic solution gives a red colour with ferric chloride, and its *barium* salt crystallises in small needles containing $4\text{H}_2\text{O}$. When heated, the diethyl salt yields carbon dioxide, the triethyl salt described above, and *m*-hydroxyruvitic acid, melting and decomposing at $295\text{—}298^\circ$, and when esterified by Fischer and Speier's method (*Abstr.*, 1896, i, 201), it yields 15 per cent. of the triethyl ester. From this behaviour, no definite conclusion can be drawn as to the constitution of the diethyl salt by employing the Victor Meyer rule.

The *monoethyl salt*, $\text{OH}\cdot\text{C}_6\text{HMe}(\text{CO}_2\text{Et})(\text{CO}_2\text{H})_2 + \text{H}_2\text{O}$, is obtained when the sodium derivative of the triethyl ester is boiled with an equivalent of sodium hydroxide solution and precipitated with acid; it crystallises from hot water in long, flat needles readily soluble in alcohol or ether; in the anhydrous form, it melts and decomposes at 224° .

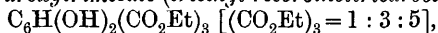
4-Hydroxy-2-methyltrimesic acid, obtained when any one of the three ethyl esters is boiled with an excess of alkali, crystallises from water in short, hard needles containing $2\text{H}_2\text{O}$ and dissolves readily in alcohol. When the anhydrous acid is heated, it melts at 257° and evolves a gas; it then solidifies and melts a second time at 280° . When heated with an excess of phosphorus pentachloride and then treated with water, the original acid is obtained; all attempts to replace the phenolic OH group by chlorine were fruitless. The *mono-sodium salt*, $\text{C}_{10}\text{H}_7\text{O}_7\text{Na} + 3\text{H}_2\text{O}$, is sparingly soluble in water, but the di- and tri-sodium salts readily dissolve.

Triethyl 4-ethoxy-2-methyltrimesate, $\text{OEt}\cdot\text{C}_6\text{HMe}(\text{CO}_2\text{Et})_3$, is a pale yellow oil which decomposes when distilled, and does not solidify in ice and salt. The *monoethyl salt*, obtained when the triethyl ester is boiled with dilute sodium hydroxide, crystallises from boiling water in prisms melting at 195° . Its constitution is probably $[(\text{CO}_2\text{H})_2 : \text{CO}_2\text{Et} : \text{Me} : \text{OEt} = 1 : 5 : 3 : 2 : 4]$. *4-Ethoxy-2-methyltrimesic acid*, $\text{OEt}\cdot\text{C}_6\text{HMe}(\text{CO}_2\text{H})_3$, crystallises from moderately dilute aqueous solutions in nodular masses of small needles containing $1\text{H}_2\text{O}$, but is

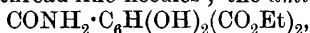
deposited from concentrated aqueous solutions as hard, anhydrous crystals melting at 242—243°.

When a cold aqueous solution of hydroxymethyltrimesic acid is treated with slight excess of bromine water and the product recrystallised from hot benzene, small needles of 2 : 6-dibromo-3-hydroxy-4-toluic acid, $\text{OH}\cdot\text{C}_6\text{HMeBr}_2\cdot\text{CO}_2\text{H}$, are deposited, whilst Claus' tribromometacresol (Abstr., 1889, 389) remains in solution. When the acid is brominated in acetic acid solution, the only product is the dibromohydroxytoluic acid; it crystallises from dilute alcohol in colourless needles melting at 233—234°, and is identical with the acid obtained by brominating 3-hydroxy-4-toluic acid.

Triethyl dihydroxytrimesate (triethyl resorcinoltricarboxylate),



is also obtained when ethyl acetonedicarboxylate is condensed with ethyl ethoxymethylenemalonate in the presence of sodium ethoxide (compare preceding page); it crystallises from alcohol in colourless needles melting at 104—105°, is readily soluble in benzene, toluene, or hot alcohol, and its alcoholic solution is turned red by ferric chloride. When boiled with sodium hydroxide (1 equivalent), it is converted into the *diethyl* salt, which crystallises from aqueous alcohol in small needles containing $1\text{H}_2\text{O}$; the anhydrous compound melts at 150—151°, and is readily soluble in alcohol; the *sodium diethyl* salt, $\text{C}_{13}\text{H}_{13}\text{O}_8\text{Na}$, crystallises in long, thread-like needles; the *amide*,



crystallises from alcohol in colourless needles melting at 218—219°, and when hydrolysed with aqueous sodium hydroxide, is converted into the *monamide* of dihydroxytrimesic acid, $\text{CONH}_2\cdot\text{C}_6\text{H}(\text{OH})_2(\text{CO}_2\text{H})_2$, which melts and decomposes at about 245°, is practically insoluble in all the ordinary organic solvents, and yields *alkali* salts which are readily soluble in water; the *barium* salt, $\text{C}_9\text{H}_5\text{O}_7\text{NBa} + 3\text{H}_2\text{O}$, crystallises from water in small needles. Senhofer and Brunner's α -resorcinoldicarboxylic acid (Abstr., 1881, 265) is formed when the ethyl tricarboxylate is boiled with excess of caustic soda and mixed with a large excess of hydrochloric acid; it melts at 304—305°, not at 276°. When esterified by Fischer and Speier's method, it yields a *monoethyl* salt melting at 202—203°, together with a minute quantity of the *diethyl* ester, which crystallises in long, flat needles melting at 137°. The constitution of the dicarboxylic acid is uncertain. J. J. S.

p-Anisaldoximes. By HECTOR R. CARVETH (*Jour. Phys. Chem.*, 1899, 3, 437—451).—*p*-Anisaldoxime exists in two modifications, the α - and β -forms, melting at 63° and 132° respectively, but the melting point depends on the rate of heating, being lower in each case if it is slow. This is due to tautomeric changes, and both compounds, if maintained above the melting point for some time, form a mixture with a melting point of 54·2°, which is hence the triple point, that is, the melting point of the equilibrium mixture of the two varieties. The eutectic point appears about 0·2° lower and on the side of the β -modification, so that the minimum melting point can only be reached by starting with the β -modification. The author finds that only the β -hydrochloride, melting at 129·5°, exists, a result at variance

with those of Hantzsch (Abstr., 1893, i, 411); by the addition of hydrogen chloride, the equilibrium temperature is raised to about 55°. In benzene and toluene solutions, the change proceeds very slowly even at the boiling point; it is never reached in aniline or alcohol solutions (compare Brühl, Abstr., 1899, i, 735). Owing to this, benzene is the best medium for separating the oximes by fractional crystallisation. The author adds examples of cases where the melting point of compounds have been stated to vary with the rate of heating, and points out that, in these cases, it is probable that isomerides may exist and are formed.

L. M. J.

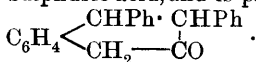
Distillation of Dypnone. By MICHEL AMEYE (*Chem. Centr.*, 1899, ii, 96—97; from *Bull. Acad. roy. Belg.*, 1899, 227—240).—Dypnone, $\text{CMePh}:\text{CH}:\text{COPh}$, is the first product of the condensation of acetophenone to form triphenylbenzene. By the action of heat on dypnone, (1) a volatile product, (2) diphenylfurfuran, and (3) triphenylbenzene are formed. According to Delacre (*Bull. Acad. roy. Belg.*, [iii], 26), the triphenylbenzene is produced by the action of styrene on diphenylfurfuran with elimination of water. The products of the reaction, however, after the acetophenone and benzaldehyde have been removed, do not yield styrene, but a hydrocarbon which combines energetically with bromine and distils at 140—165°. Allylbenzene is probably present. By heating the product of the reaction at 280°, ethylbenzene is obtained.

E. W. W.

Pseudodicotoin. By OSWALD HESSE (*Annalen*, 1899, 309, 95—96. Compare Abstr., 1895, i, 110; also Ciamician and Silber, Abstr., 1897, i, 57).—Pseudodicotoin, $\text{C}_{25}\text{H}_{20}\text{O}_7$, separates from a mixture of ether and petroleum in crystalline aggregates, whilst dicotoin is deposited in leaflets. When the ethereal solution is submitted to prolonged treatment with sodium carbonate, the latter dissolves cotoin, whilst the ether, on evaporation, deposits hydroxyphenylcoulalin.

M. O. F.

Condensation of Dibenzyl Ketone with Benzaldehyde. By GUIDO GOLDSCHMIEDT and GUSTAV KNÖPFER (*Monatsh.*, 1899, 20, 734—754).—The hydrogen chloride additive product of benzylidene-dibenzyl ketone (Abstr., 1899, i, 141) easily dissolves in a strong alcoholic solution of potassium hydroxide, and on pouring this solution into water a compound, $\text{C}_{22}\text{H}_{18}\text{O}$, is obtained; this crystallises from alcohol in leaflets melting at 86°, does not form an additive compound with bromine, gives a deep green coloration with strong sulphuric acid, and is probably 1 : 2-diphenyltetrahydro- β -naphthenone,



The oxime crystallises from alcohol in prisms melting at 158°, and yields only tarry products when treated with acetic anhydride. Often, instead of the above substance, a violet coloured mass is obtained, which when washed with ether leaves an isomeric compound, $\text{C}_{22}\text{H}_{18}\text{O}$; this crystallises from alcohol in needles melting at 162—163°. The formation of the oxime of chlorobenzylbenzyl methyl ketone (*loc. cit.*)

requires long boiling; with only half an hour's boiling, a *compound*, $C_{32}H_{31}O_2NCl_2$, melting at 130° is obtained, which is probably an additive compound of the ketone and its oxime.

If the alkaline filtrate obtained in the preparation of 1:2-diphenyl-tetrahydro- β -naphthenone is acidified, a monobasic *acid*, $C_{22}H_{20}O_2$, is precipitated; this forms lustrous leaflets melting at 154 — 155° , and in neutral solution gives precipitates with solutions of silver nitrate, copper sulphate, and ferric chloride. It is saturated and forms a *methyl* ester melting at 107° , and an *ethyl* ester melting at 50° . It is probably $\alpha\beta\gamma$ -triphenylbutyric acid.

Dibenzyl ketone can be condensed with benzaldehyde in the presence of dilute potassium hydroxide solution to form a *compound*, $C_{29}H_{26}O_3$; this is very sparingly soluble in all cold, but easily soluble in most hot media, and crystallises in woolly needles melting at 144 — 147° . It is probably $\alpha\beta\delta\epsilon$ -tetraphenyl- γ -pentanone- $\alpha\epsilon$ -diol, $CO(CHPh\cdot CHPh\cdot OH)_2$. It, however, does not form an oxime, and is not changed by boiling with acetic anhydride. When heated at 150° , benzaldehyde is eliminated and a *ketone*, $C_{22}H_{20}O_2$, formed; this melts at 97° , and is probably $\alpha\gamma\beta$ -triphenyl- γ -butenone- α -ol, $OH\cdot CHPh\cdot CHPh\cdot CO\cdot CH_2Ph$; its oxime crystallises from alcohol in small needles melting at 140° .

R. H. P.

Condensation Products of *o*-Aldehydic Acids with Ketones.

By HUGO LUDWIG FULDA (*Monatsh.*, 1899, 20, 698—716).—The properties of the substances obtained by Goldschmidt (Abstr., 1892, 179) and Hamburger (Abstr., 1899, i, 142) by the condensation of opianic acid and phthalaldehydic acid with acetone and acetophenone, have been studied, in order to determine whether they are acids or lactones. These substances are all insoluble in sodium hydrogen carbonate solution, but form salts gradually when in contact with an alkali hydroxide. According to Hantzsch's nomenclature (Abstr., 1899, i, 400), they can be designated "pseudo-acids." The figures obtained by the gradual titration of phthalidimethyl ketone, meconinidimethyl ketone, phenyl phthalidimethyl ketone, and phenyl meconinemethyl ketone with potassium hydroxide in aqueous alcoholic solution are given.

The alkali salts of these compounds were prepared by boiling them with potassium carbonate in absolute alcoholic solution until the evolution of carbon dioxide ceased, filtering, and evaporating in a desiccator. The *potassium* salt of meconinidimethyl ketone has a deep yellow colour, whilst the *potassium* salt of phenyl phthalidimethyl ketone forms long, silky needles, which are almost colourless. These salts undergo a gradual decomposition when titrated with decinormal hydrochloric acid, helianthin being used as an indicator. The investigations show that these substances possess the lactone form owing to an intramolecular transformation of the true acids, which are primarily formed in the condensation.

In order to decide whether the acids primarily formed are unsaturated acids or hydroxy-acids, the following methyl derivatives were prepared by heating the potassium salts of these substances with methyl iodide and methyl alcohol in a sealed tube: the *methyl* derivative of phthalidimethyl ketone, $C_{12}H_{12}O_3$, is a yellow oil; the *methyl* derivative of

meconinedimethyl ketone, $C_{14}H_{16}O_5$, forms yellow needles melting at $72-73^\circ$; the *methyl* derivative of phenyl phthalidemethyl ketone, $C_{17}H_{12}O_3$, is a yellowish oil; the *methyl* derivative of phenyl meconine-methyl ketone, $C_{19}H_{18}O_5$, forms yellowish needles melting at $97-98^\circ$. The formation of these compounds shows that the substances primarily formed in the condensations in question are unsaturated acids.

The paper concludes with a discussion of the probable formulæ of some of Hamburger's compounds. R. H. P.

Isomeric Forms of Dibenzoylmethane. By JOHANNES WISLICENUS [with BRUNO LÖWENHEIM, PAUL SCHMIDT, and HARRY EDWARD WELLS] (*Annalen*, 1899, 308, 219—263).—When benzylideneacetophenone, $CHPh:CH \cdot CPh$, is dissolved in chloroform and treated with bromine (1 mol.), the *dibromide* is precipitated; this crystallises from alcohol and melts at $156.5-157.5^\circ$. *Bromobenzylideneacetophenone*, $CBrPh:CH \cdot CPh$, prepared by heating the dibromide with alcoholic potassium acetate, crystallises in slender, yellow prisms, and melts at $43-44^\circ$. Hot alcoholic potash converts these bromo-compounds into a mixture of two isomerides, $C_{15}H_{12}O_2$, of which the less readily soluble is the substance known as dibenzoylmethane (von Baeyer and Perkin, *Abstr.*, 1884, 64). Closer investigation, however, has shown that the more readily soluble isomeride is the actual dibenzoylmethane, $CH_2(CPh)_2$, whilst the substance hitherto known by this name is the *keto-enolic* modification, or *α -hydroxybenzylideneacetophenone*, $OH \cdot CPh:CH \cdot CPh$; the latter is readily produced from the former, but the converse reaction is not complete.

Dibenzoylmethane, the new compound under an old name, is obtained quantitatively by heating bromobenzylideneacetophenone with alcoholic soda (1 mol.), and melts simultaneously with the isomeride at $77-78^\circ$; in chemical behaviour, it closely resembles the keto-enolic modification, but differs from that substance in crystalline form, and in its greater solubility in organic media. It is insoluble in caustic alkalis, and is indifferent towards ferric chloride and copper acetate, whilst *α -hydroxybenzylideneacetophenone* dissolves readily in dilute alkalis, develops immediately an intense, violet-red coloration with ferric chloride, and yields, with copper acetate, a crystalline, greyish-green *copper* derivative, $(C_{15}H_{11}O_2)_2Cu$.

Although the isomerides are indifferent towards acetic anhydride and glacial acetic acid, phenylcarbimide combines with the keto-enolic modification, but not with dibenzoylmethane; the *urethane*, $NHPh \cdot CO_2 \cdot CPh:CH \cdot CPh$, crystallises from alcohol in minute needles and melts at 181° .

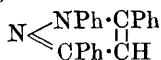
The two forms behave alike towards dilute nitric acid, yielding benzoic acid and carbon dioxide, but potassium permanganate oxidises dibenzoylmethane much more slowly than *α -hydroxybenzylideneacetophenone*, benzoic and benzoylformic acids being produced.

Both modifications boil at $219-221^\circ$ under 18 mm. pressure, without undergoing change. As already indicated, dibenzoylmethane is the more readily soluble, dissolving in 11.6 parts of alcohol at 19.5° , whilst *α -hydroxybenzylideneacetophenone* requires 22.5 parts. Concentrated sulphuric and hydrochloric acids rapidly convert

dibenzoylmethane into the keto-enolic modification, and the same change is effected by alkalis, but in this case is attended with resolution into acetophenone and benzoic acid. The two modifications behave alike towards bromine, yielding bromodibenzoylmethane and dibromodibenzoylmethane (compare Neufville and von Pechmann, Abstr., 1891, 318).

3 : 5-Diphenylisoxazole, $\text{CH} \begin{smallmatrix} \text{CPh} \cdot \text{O} \\ \text{CPh} \cdot \text{N} \end{smallmatrix}$, prepared by heating alcoholic solutions of the isomerides with hydroxylamine hydrochloride, crystallises from carbon disulphide in long, six-sided prisms and melts at $140.5-141^\circ$; it is indifferent towards concentrated hydrochloric acid at 200° , and merely volatilises when fused with moist alkali, but hydriodic acid at 150° attacks it slowly, forming benzoic acid. The *oxime*, $\text{C}_{15}\text{H}_{13}\text{O}_2\text{N}$, is produced when free hydroxylamine acts on an alcoholic solution of α -hydroxybenzylideneacetophenone or its isomeride, and crystallises in lustrous prisms melting at 165° ; the *compound*, $\text{C}_{22}\text{H}_{18}\text{O}_3\text{N}_2$, obtained from the oxime by the action of phenylcarbimide, crystallises in needles, and melts at 132° .

The two modifications behave alike towards hydrazine and phenylhydrazine, yielding 3 : 5-diphenylpyrazole, $\text{N} \begin{smallmatrix} \text{NH} \cdot \text{CPh} \\ \text{CPh} \cdot \text{CH} \end{smallmatrix}$ (Knorr and Duden, Abstr., 1893, i, 231), and 1 : 3 : 5-triphenylpyrazole,

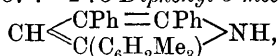


(Knorr and Laubmann, Abstr., 1888, 725), respectively. Semicarbazide converts the isomerides into the *semicarbazone* of α -hydroxybenzylideneacetophenone, which crystallises in thin plates, and decomposes at 187° , if heated slowly, melting at 205° when the temperature is raised more rapidly; 3 : 5-diphenylpyrazole is produced at the same time, and also results from the semicarbazone under the influence of concentrated hydrochloric acid in alcohol. M. O. F.

Potassium Cyanide as a Condensing Agent. By ALEXANDER SMITH (*Amer. Chem. J.*, 1899, 22, 249—256. Compare Trans., 1890, 643).—*Desyl- α -acetonaphthone*, $\text{COPh} \cdot \text{CHPh} \cdot \text{CH}_2 \cdot \text{CO} \cdot \text{C}_{10}\text{H}_7^a$, prepared by boiling a solution of α -acetonaphthone and benzoin in 50 per cent. alcohol containing a small quantity of potassium cyanide for 1 hour, crystallises from benzene on adding light petroleum in stellar aggregates of white needles and melts at 151° ; when dissolved in concentrated sulphuric acid, it yields 2 : 3-diphenyl-5- α -naphthylfurfuran, $\begin{smallmatrix} \text{CPh} = \text{CPh} \\ | \\ \text{CH} : \text{C}(\text{C}_{10}\text{H}_7) \end{smallmatrix} > \text{O}$, which crystallises from light petroleum in slender, white needles and melts at 96° . 2 : 3-Diphenyl-5- α -naphthylpyrrole, $\begin{smallmatrix} \text{CPh} = \text{CPh} \\ | \\ \text{CH} : \text{C}(\text{C}_{10}\text{H}_7) \end{smallmatrix} > \text{NH}$, prepared by heating the naphthone with alcoholic ammonia at $200-220^\circ$ for 8 hours, crystallises from alcohol in white needles and melts at 122° ; the corresponding *thiophen* derivative, obtained by heating desyl- α -acetonaphthone with phosphorus pentasulphide, melts at 93° .

Desyl-β-acetonaphthone, prepared from *β*-acetonaphthone, crystallises from benzene in white needles and melts at 155°.

When benzaldehyde is heated with a little powdered potassium cyanide for 3/4 hour at 150°, a good yield of benzoin is obtained; potassium hydroxide did not give benzoin by this method. Desylacetophenone and desyl-*α*-acetonaphthone, however, are easily prepared by heating benzoin and the corresponding ketone with either potassium cyanide or hydroxide at 150° for 20 minutes. Moreover, by this process, *desylacetomesitone*, $\text{COPh} \cdot \text{CHPh} \cdot \text{CH}_2 \cdot \text{CO} \cdot \text{C}_6\text{H}_2\text{Me}_3$, which cannot be prepared by heating benzoin and acetomesitone with potassium cyanide in alcoholic solution, is readily obtained; it crystallises from alcohol in white needles, melts at 115°, and when dissolved in cold concentrated sulphuric acid yields the corresponding *furfuran* derivative which crystallises from methyl alcohol in stellar aggregates of needles and melts at 87°. 2 : 3-*Diphenyl-5-mesitylpyrrole*,



obtained by heating desylacetomesitone with alcoholic ammonia for 7 hours at 230—240°, forms white needles and melts at 188°.

The action of potassium cyanide on a fused mixture of benzyl cyanide and benzoin gives rise, not to the simple condensation product expected, but to the compound, $\text{OH} \cdot \text{CHPh} \cdot \text{CPh}(\text{CHPh} \cdot \text{CN})_2$, obtained by Schleussner (*Diss. Frankfurt*, 1893), on heating the same substances in alcoholic solution; *α*-phenylcinnamionitrile (Frost, *Abstr.*, 1889, 597) and diphenylsuccinonitrile are also formed. W. A. D.

Preparation and Configuration of the Six Isomeric Inactive Benzylidenebisacetylacetones. By ROBERT SCHIFF (*Annalen*, 1899, 309, 206—232).—Under conditions described in the original paper, the author has isolated the six isomeric inactive benzylidenebisacetylacetones and determined their configuration.

The *diketonic* modification, $\text{CHPh}(\text{CHAc} \cdot \text{COMe})_2$, crystallises from a mixture of benzene and petroleum in slender, silky needles, and melts at 163°; the alcoholic solution is indifferent towards ferric chloride, even after boiling, or after an interval of many days.

The *trans-keto-enolic* modification, $\text{COMe} \cdot \text{CHAc} \cdot \text{CHPh} \cdot \text{CAc} \cdot \text{CMe} \cdot \text{OH}$, obtained by repeatedly treating with boiling benzene the benzylidenebisacetylacetone (melting at 168°) described by Knoevenagel (*Abstr.*, 1895, i, 50), crystallises from benzene in leaflets, and melts at 182—183°, when it becomes deep red; the cold, alcoholic solution with ferric chloride gradually develops a red coloration, which is produced immediately when the liquid is warmed. The specimen melting at 168° obtained by Knoevenagel's method, is probably an allelotropic mixture (Knorr, *Abstr.*, 1899, i, 673) of the *trans-keto-enolic* modification with the *trans-trans*-dienolic form (see below). The *trans-keto-enolic* modification is very labile, and in the course of two months becomes converted spontaneously into the allelotropic mixture, this change being effected also by a single crystallisation from boiling alcohol.

The *cis-keto-enolic* modification crystallises from alcohol in slender, lustrous needles, and melts at 123°; the cold solution is indifferent towards ferric chloride, even after a long interval, but when boiled, at

once develops colour. It dissolves in cold, dilute caustic soda, and when the solution is acidified, a mixture of the original substance with the *cistrans*-dienolic modification is produced; an allelotropic mixture of these two forms, melting at 110—112°, is obtained on fusing the *cis*-keto-enolic derivative.

The *transtrans*-dienolic modification, $\text{CHPh}(\text{CHAc} \cdot \text{CMe} \cdot \text{OH})_2$, obtained by the action of alcoholic sodium ethoxide on the *trans*-keto-enolic form, crystallises from hot petroleum in aggregates of long, colourless prisms, and melts at 91—92°, when it undergoes ketonisation in part, yielding the allelotropic mixture which melts at 168°; the alcoholic solution immediately develops a deep carmine red coloration with ferric chloride. The *anhydride*, $\text{C}_{17}\text{H}_{18}\text{O}_3$, is a colourless, viscous oil which is indifferent towards ferric chloride; when treated with 5 per cent. caustic soda, acetic acid is eliminated, and 5 : 3-phenylmethyl- Δ^2 -cyclohexenone, $\text{CHPh} \begin{smallmatrix} \text{CH}_2 \cdot \text{CMe} \\ \text{CH}_2 - \text{CO} \end{smallmatrix} \text{CH}$, produced (compare Knoevenagel, *loc. cit.*)

The *cistrans*-dienolic modification prepared from the *cis*-keto-enolic derivative by the action of alcoholic sodium ethoxide, melts at 93—94° to a clear liquid which becomes turbid at 95°, and then crystalline, melting finally at 118—119°; after an interval, if allowed to cool, the same specimen melts at 110—112°, which temperature undergoes no further change, being that which the allelotropic mixture of the *cis*-keto-enolic and *cistrans*-dienolic derivatives undergoes fusion. Ferric chloride immediately develops an intense wine-red coloration with this form of benzylidenedisacetylacetone.

The *ciscis*-dienolic modification occurs in the mother liquor of the initial product of the condensation of benzaldehyde with acetylacetone, and crystallises from benzene in large, lustrous prisms melting at 125—126°; it immediately develops a deep carmine-red coloration with ferric chloride. It is a stable substance, and may be heated at the melting point for some time without changing into the diketonic form melting at 163°; this conversion is brought about, however, by fuming hydrochloric acid.

Further confirmation of the proposed configuration of the isomerides is afforded by the conversion of the *cis*-keto-enolic modification into the *trans*-keto-enolic form under the influence of hot, fuming hydrochloric acid, and the transformation of diketobenzylidenedisacetylacetone into the *transtrans*-dienolic derivative by the agency of alcoholic sodium ethoxide. M. O. F.

Compounds from Rhubarb, and Allied Substances. By OSWALD HESSE (*Annalen*, 1899, 309, 32—75. Compare Abstr., 1895, i, 292 and 299).—By a method of treatment which is fully described in the original paper, Chinese rhubarb yields chrysophanic acid, emodin, rhabarberone, and rhein.

Chrysophanic acid, $\text{C}_{15}\text{H}_{10}\text{O}_4$, crystallises from benzene, alcohol, or glacial acetic acid in yellow leaflets, and melts at 186—188°; the substance has been previously described as melting at different temperatures between 154° and the true point of fusion, the presence of varying amounts of methylchrysophanic acid being the cause of the

uncertainty. It dissolves in 1989 parts of absolute alcohol at 15° , and the solution develops a dark reddish-brown coloration with ferric chloride, becoming cherry-red with bleaching powder. A cherry-red precipitate of the *barium hydroxide* derivative, $C_{15}H_{10}O_4 \cdot Ba(OH)_2 + H_2O$, is obtained on adding aqueous barium hydroxide to a dilute solution in alcohol. The *acetyl* derivative crystallises from glacial acetic acid in yellow needles, and melts at 152° ; the alcoholic solution develops a brownish-red coloration with ferric chloride, and becomes red when treated with caustic potash. Chrysophanic acid dissolves less readily in ammonia than Liebermann represents; the product of the action of the cold alkali is aminochrysophanic acid.

Rhabarberone, $C_{15}H_{10}O_5$, crystallises from alcohol in yellow leaflets, and melts at 212° ; the alcoholic solution develops a brownish-red coloration with ferric chloride, and an aqueous solution of alkali carbonate dissolves the substance, developing a purple coloration. Hydriodic acid converts it into *rhabarberohydroanthrone*, $C_{15}H_{12}O_4$, without eliminating methyl iodide; it crystallises in yellow leaflets and fuses to a black mass at $215-220^{\circ}$.

Rhein, $C_{15}H_{10}O_6$, melts at $262-265^{\circ}$, and when dissolved in alcohol develops an intense reddish-brown coloration with ferric chloride; acetic anhydride converts it into the *diacetyl* derivative, $C_{15}H_8O_4(OAc)_2$.

Austrian rhubarb contains chrysophanic acid, contaminated as usual with methylchrysophanic acid, and *rhapontin*, $C_{22}H_{24}O_9$, which crystallises from water in yellowish prisms, and melts, decomposing at 235° . Rhapontin is indifferent towards ferric chloride, and is neutral to litmus, but the aqueous solution becomes acid when boiled; it contains one methoxyl group, dissolves readily in alkalis and alkali carbonates, and forms the *lead* derivative, $C_{21}H_{20}O_9Pb_2$. The *tetracetyl* derivative melts at 102° . Rhapontin also occurs in English rhubarb, and the chrysophanic acid derived from this source melts at 188° , and contains only a small proportion of methylchrysophanic acid.

It has been stated by the author (Abstr., 1896, i, 573) that the root of *Rumex nepalensis* yields rumicin, nepalin, and nepodin, of which the first-named had the empirical formula of chrysophanic acid. It now transpires that rumicin is chrysophanic acid, uncontaminated with methylchrysophanic acid, whilst nepalin is identical with nepodin, $C_{18}H_{16}O_4$.

The root of *Rumex palustris* contains chrysophanic acid and nepodin, which are also present in *Rumex obtusifolius*, along with *lapodin*, $C_{18}H_{16}O_5$, which crystallises from alcohol in yellow needles and melts at 206° , when it decomposes. An alcoholic solution of lapodin develops a dark brown or greenish-brown coloration with ferric chloride, and hydriodic acid does not eliminate a methyl group.

Araroba powder, prepared from a Brazilian wood, is employed in the treatment of skin diseases, and was formerly known as Bahia powder, Goa powder, and chrysarobin. Liebermann and Seidler (*Annalen*, 1882, 212, 29) have employed the last name for indicating a yellow, crystalline compound occurring in Goa powder, and sold in Germany as "chrysophanic acid," although it is quite free from true chrysophanic acid. Owing to the confusion to which this contradiction gives rise, the author has investigated commercial "chrysophanic acid" and araroba powder.

Chrysarobin, obtained by extracting araroba powder with ether,

melts at 174° , and has the formula $C_{15}H_{12}O_3$, and not $C_{30}H_{24}O_7$ (compare Liebermann and Seidler); it is usually associated with methylchrysarobin in the proportion 2:1, and for this reason the melting points of different specimens vary widely. Ferric chloride develops a deep brownish-red coloration in the alcoholic solution, and dilute potash dissolves it slowly, forming a yellowish-red solution with feeble green fluorescence; concentrated sulphuric acid also forms a yellowish-red solution, becoming dark brown when warmed. Glacial acetic acid polymerises chrysarobin to *dichrysarobin*, which is readily soluble, and becomes red when treated with dilute potash and exposed to air. Fuming hydrochloric acid at $100-140^{\circ}$ eliminates a methyl group from methylchrysarobin, and gives rise to chrysophanohydroanthrone, which is isomeric with chrysarobin. Chrysophanohydroanthrone, $C_{15}H_{12}O_3$, prepared alike from chrysarobin and chrysophanic acid by the action of hydriodic acid, melts at $205-210^{\circ}$, and when mixed with dilute potash and submitted to the action of a current of air, yields chrysophanic acid; the *diacetyl* derivative crystallises from glacial acetic acid in pale yellow needles melting at $238-240^{\circ}$, and is indifferent towards ferric chloride.

Chrysarobin yields three acetyl derivatives, which do not produce colour with ferric chloride. The *monoacetyl* derivative, prepared by the action of boiling acetic anhydride, crystallises from glacial acetic acid in yellow leaflets, and melts at $188-190^{\circ}$, the solutions in alcohol and acetic acid exhibiting a blue fluorescence. The *diacetyl* derivative, formed when acetic anhydride acts on chrysarobin during 6 hours, crystallises from glacial acetic acid in yellow, rhombic leaflets, and melts at 216° ; a pharmaceutical preparation called *lenirobin* appears to consist of this substance mixed with β -*diacetylchrysarobin*, which crystallises from alcohol in yellow needles and melts at $265-270^{\circ}$. The *triacetyl* derivative, obtained by heating chrysophanohydroanthrone with acetic anhydride and sodium acetate during 1 hour, melts at 125° ; if the treatment is prolonged, *hexacetyldichrysarobin*, $C_{30}H_{18}(OAc)_6$, is formed. *Eurobin* is a pharmaceutical preparation composed principally of diacetyldichrysarobin.

The constitution of the foregoing compounds is discussed in the paper. M. O. F.

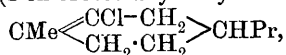
Naphthapurpurin (Trihydroxy- α -naphthaquinone). By GEORGE F. JAUBERT (*Compt. rend.*, 1899, 129, 684-686).—Naphthazarin, on oxidation with manganese dioxide and sulphuric acid, gives *trihydroxy- α -naphthaquinone*, $[OH \cdot OH \cdot OH :: 1:2:4]$, which, from its analogy to purpurin, the author terms *naphthapurpurin*. This forms reddish-brown needles, which can be melted or sublimed, and are sparingly soluble in cold, but very easily in hot water, forming a yellowish-brown solution, which is decolorised by zinc dust with probable formation of pentahydroxynaphthalene. Naphthapurpurin possesses well marked dyeing properties; with an aluminium mordant, cotton is dyed a carmine red, and with a chromium mordant wool is dyed a dull brown. Naphthapurpurin forms acetyl and benzoyl derivatives. H. R. LE S.

The Carvone Series. By AUGUST KIAGES and A. KRAITH (*Ber.*, 1899, 32, 2550-2563).—By converting the members of the carvone

series into 2-chlorocymene it is shown that the ketone group in carvone compounds occupies the ortho-position to the methyl group.

2-Chlorohexahydrocymene, obtained by the action of phosphorus pentachloride on tetrahydrocarveol, boils at 85° under 20 mm. pressure, has a sp. gr. 0.935 at 18°, and a refractive index n_D 1.46179.

2-Chloro- Δ^1 -terpene (2-chlorotetrahydrocymene),



prepared by the action of phosphorus pentachloride on carvomenthone boils at 210—211° under ordinary pressure, and at 112° under 20 mm. pressure; it has a sp. gr. 1.001 at 18°, and an index of refraction n_D 1.52301. When treated with a molecular proportion of bromine, it yields 2-chlorobromotetrahydrocymene, $\text{C}_{10}\text{H}_{16}\text{ClBr}$, which is an oil having a sp. gr. 1.423 at 18°; on boiling with quinoline, it loses the elements of hydrogen bromide, 2-chlorodihydrocymene, $\text{C}_{10}\text{H}_{15}\text{Cl}$, being formed as a colourless oil boiling at 210—212°, and having a sp. gr. 1.01 at 18° and a refractive index n_D 1.51202. The action of bromine on this compound gives rise to 2-chlorobromodihydrocymene, $\text{C}_{10}\text{H}_{14}\text{ClBr}$, which is a heavy, brown oil of sp. gr. 1.543 at 18°, and when treated with quinoline yields 2-chlorocymene. The authors find the melting point of 2-chlorocymenesulphonic acid to be 125°, the value formerly obtained by Jünger and Klages being 135°, which is regarded as erroneous.

Carvone dichloride, $\text{CMe} \begin{array}{c} \text{CCl}=\text{CH} \\ \text{CH}_2 \cdot \text{CH}_2 \end{array} > \text{CH} \cdot \text{CMe}_2\text{Cl}$, is a slightly coloured oil having a sp. gr. 1.188 at 18°; it is converted into 2-chlorocymene when heated either with quinoline or with dilute sulphuric acid under pressure, or with methyl alcoholic potash. 2-Chlorocymene is obtained directly from carvone by adding the latter to phosphorus pentachloride covered with a layer of light petroleum, and 2-bromocymene is obtained in a similar manner from carvone and phosphorus pentabromide. With carvone and phosphorus triiodide, an oil is obtained which, either when treated with methyl alcoholic potash or when distilled with quinoline, gives rise to a product free from iodine. Eucarvone also yields 2-chlorocymene when treated with phosphorus pentachloride. Owing to the good yields obtained, 2-chloro- and 2-bromo-cymenes may be conveniently prepared by the above method.

2-Chloro- $\Delta^{1,3}$ -terpadiene, $\text{CMe} \begin{array}{c} \text{CCl}-\text{CH} \\ \text{CH}_2 \cdot \text{CH}_2 \end{array} > \text{CPr}^{\beta}$, obtained from carvenone and phosphorus pentachloride, is a colourless oil which boils under ordinary pressure at 207—208° and under 16 mm. pressure at 105°, has a sp. gr. 1.023 at 20° and a refractive index n_D 1.51620; treatment with sulphuric acid reconverts it into carvenone. The 2-chlorobromoterpadiene, $\text{C}_{10}\text{H}_{14}\text{ClBr}$, on distillation with quinoline, yields 2-chlorocymene.

Dihydrocarvone yields a chloride, $\text{C}_{10}\text{H}_{15}\text{Cl}$, which boils at 208° under ordinary pressure and at 105—106° under 16 mm. pressure, has a sp. gr. 1.025 at 18° and a refractive index n_D 1.51622; its physical constants point to its identity with the chloride obtained from carvenone.

Dihydroeucarveol acetate, $\text{C}_{12}\text{H}_{20}\text{O}_2$, boils at 223—224° (corr.), has a

sp. gr. 0.951 at 20°, and a refractive index n_D 1.46315; the isomeric *dihydrocarveol acetate* is a pleasant ethereal-smelling oil which boils at 231–232° and has a sp. gr. 0.947 at 18°. From neither of these acetates is acetic acid removed by boiling with quinoline.

Dihydroeucarveol chloride, $C_{10}H_{17}Cl$, boils at 85° under 20 mm. pressure; it does not yield 2-chlorocymene, but is converted into Baeyer's euterpene (Abstr., 1898, i, 676).

On treatment with phosphorus pentachloride, dihydroeucarvone yields a *chloride*, $C_{10}H_{15}Cl$, boiling at 92–93° under 18 mm. pressure, and having a sp. gr. 1.02 at 18° and a refractive index n_D 1.51250. On treating this chloride with excess of bromine and distilling the compound thus obtained with quinoline, two products were formed, one does not contain chlorine and the other, $C_{10}H_{13}Cl$, is isomeric with 2-chlorocymene, but does not yield a sulphonic acid and is oxidised by cold permanganate.

T. H. P.

Pulegone and Methylhexanone. By AUGUST KLAGES (*Ber.*, 1899, 32, 2564–2569).—Pulegone in acetic acid solution absorbs bromine, giving a bromide which, when heated, loses hydrogen bromide and yields methylcyclohexanone and *m*-cresol.

3-Chloro- $\Delta^{(4:8)}$ -terpadiene, $CHMe \begin{smallmatrix} \text{CH}=\text{CCl} \\ \text{CH}_2 \cdot \text{CH}_2 \end{smallmatrix} C:Me_2$, obtained by the action of phosphorus pentachloride on pulegone, is a colourless oil, boils at 101° under 25 mm. pressure, has a sp. gr. 0.983 at 19°, and a refractive index n_D 1.49928. With excess of bromine, it yields a *tetrabromo-derivative*, $C_{10}H_{11}ClBr_4$, as a dark-coloured oil; treatment of this compound with quinoline gives a product having the boiling point of chlorocymene (212–216°), which, however, does not yield a sulphonic acid. Formic acid converts the chloroterpadiene into methylcyclohexanone; a good method of preparing the latter is by the action of formic acid on pulegone.

When methylcyclohexanone is brominated, and the product heated with quinoline, *m*-cresol is obtained.

3:3-Dichlorohexahydrotoluene, $CH_2 \begin{smallmatrix} \text{CCl}_2-\text{CH}_2 \\ \text{CHMe} \cdot \text{CH}_2 \end{smallmatrix} CH_2$, is formed by the interaction of phosphorus pentachloride and methylcyclohexanone in the cold. If the mixture is not cooled, *m-chlorotetrahydrotoluene*, $C_7H_{11}Cl$, is obtained as an oil boiling at 76–79° under 29 mm. pressure and decomposing at 160–170° under ordinary pressure; it has a sp. gr. 1.021 at 18°, and a refractive index n_D 1.48891. On brominating this compound and heating with quinoline, *m*-chlorotoluene is obtained.

T. H. P.

Terpenes and Ethereal Oils: Ring Disruption and Ring Formation among Terpene Derivatives. By OTTO WALLACH (*Annalen*, 1899, 309, 1–31).—The oximes of cyclic ketones usually undergo ring disruption with great facility, yielding the nitrile of an unsaturated aliphatic acid, with an isoxime as intermediate compound; cyclic bases frequently occur as bye-products. Conversely, aliphatic unsaturated ketones may be converted into cyclic bases by reducing the oxime, adding bromine to the amine thus obtained, and withdrawing 2HBr from the product.

[With TH. BÖCKER.]—A mixture of concentrated sulphuric and glacial acetic acids converts methylhexanoneoxime into the *α-isoxime*, $C_7H_{13}ON$, melting at $104-105^\circ$, which has $\alpha_D -3.2^\circ$ in alcohol, and the *β-isoxime*, which melts at $65-66^\circ$; these compounds are distinguished from the original oxime by their solubility in water, and also by their stability towards dilute acids, which do not affect them even when boiled. The isoximes are feeble bases, and form readily soluble hydrochlorides, and compounds with alkyl iodides; their constitution is most likely expressed by the formulæ $CH_2<\begin{smallmatrix} CHMe-CH_2 \\ CH_2\cdot CH_2\cdot CO \end{smallmatrix}>NH$ and $CH_2<\begin{smallmatrix} CHMe-CH_2 \\ CH_2\cdot CH_2\cdot NH \end{smallmatrix}>CO$, but the possibility of physical isomerism is not excluded, as both forms boil at $154-155^\circ$ under 14 mm. pressure, and at $278-279^\circ$ under atmospheric pressure.

Phosphoric oxide acts vigorously on methylhexanoneoxime, producing unsaturated hydrocarbons of the aliphatic series, together with toluene, dihydrotoluene, and the nitrile of an unsaturated acid, $C_7H_{12}O_2$, probably identical with Fittig's $\beta\gamma$ -isoheptenoic acid. This acid boils at $120-121^\circ$ under 12 mm. pressure, at $219-222^\circ$ under atmospheric pressure, and has a molecular refraction 35.92 ; the amide melts at $68-70^\circ$, the calcium salt contains $1\frac{1}{2}H_2O$, and the isomeric lactone is a liquid which boils at $116-120^\circ$ under reduced pressure.

[With W. RATH.]—Methylhexanoneoxime and phosphoric oxide also give rise to a lutidine, C_7H_9N , which shows some resemblance to 2:6-dimethylpyridine. It boils at $148-156^\circ$, forms a picrate which melts at $163-164^\circ$, and a platinichloride which crystallises from alcoholic hydrochloric acid in thick plates and melts at $197-198^\circ$; the aurichloride melts at $127-128^\circ$.

Phosphoric oxide converts methylpentanoneoxime into volatile hydrocarbons, the nitrile of $\beta\gamma$ -hexenoic acid and 3-methylpyridine.

A mixture of glacial acetic and concentrated sulphuric acids transforms suberoneoxime into the *isoxime*, $C_7H_{13}ON$, which melts at 25° and boils at 156° under 8 mm. pressure; the *hydrochloride* dissolves very readily in water, and the *platinichloride* forms large crystals. Phosphoric oxide acts on the *isoxime* when heated, forming the nitrile of a heptenoic acid, $C_7H_{12}O_2$.

Thujaketoneoxime, $C_9H_{16}:NOH$, derived from methyl heptylene ketone (Abstr., 1893, i, 107), boils at $118-120^\circ$ under 15 mm. pressure. Reduction converts it into the *base*, $C_9H_{17}\cdot NH_2$, which boils at $78-79^\circ$ under 26 mm. pressure, and forms the *carbamide* melting at $104-105^\circ$. A base belonging to the pyridine series results on eliminating water from the oxime by means of concentrated sulphuric acid.

[With EUGEN VON BIRON.]—Phosphoric oxide acts vigorously on thujaketoneoxime, yielding the *base*, $C_9H_{15}N$, which boils at $180-183^\circ$, and has a sp. gr. 0.892 at 25° ; the *picrate* decomposes above 170° without melting, and the *platinichloride* melts and decomposes at 179° .

[With HERM. UMBROGROVE.]—The *base*, $C_8H_{15}\cdot NH_2$, obtained by reducing methylheptenoneoxime in alcohol with sodium, boils at $166-167^\circ$, has a sp. gr. 0.7975 at 20° , and a molecular refraction 42.47; the *picrate*, *oxalate*, and *carbamide* melt at 112° , 203° , and

118° respectively. The *hydrochloride* is hygroscopic, and yields the *platinichloride*, which melts at 165°; the *dihydrochloride* of the base, $C_8H_{16}Cl \cdot NH_2$, produced on passing hydrogen chloride into an ethereal solution of the base, $C_8H_{15} \cdot NH_2$, melts at 150°.

When bromine (1 mol.) is added to an aqueous solution of the hydrochloride, $C_8H_{15} \cdot NH_2 \cdot HCl$, the colour is destroyed, and on evaporating the solution, hydrogen bromide is evolved; caustic soda liberates from the residue the base, $C_8H_{15}N$, which boils at 145—147°, has a sp. gr. 0.838 at 20°, and a molecular refraction 39.39. The *picrate* and *oxalate* melt at 139° and 141° respectively. The constitution

of the base is expressed by one of the formulæ $CH_2 \begin{smallmatrix} \text{CH}_2 - \text{C} : \text{CMe}_2 \\ \text{CHMe} - \text{NH} \end{smallmatrix}$
and $CH_2 \begin{smallmatrix} \text{CH}_2 \cdot \text{CH} : \text{CMe}_2 \\ \text{CHMe} - \text{NH} \end{smallmatrix}$.

[With AD. GILBERT.]—Phosphoric oxide converts methylheptenone-oxime into a base, $C_8H_{15}N$, which boils at 183°; the *picrate* melts and decomposes at 149—150°, the *platinichloride* decomposes before fusion, and the *aurichloride* forms yellow needles which melt and decompose at 164—165°. M. O. F.

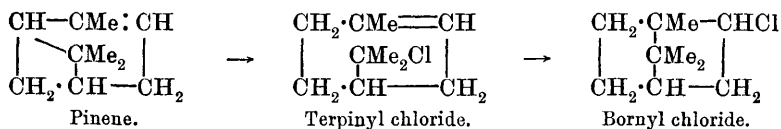
Relation of Pinene Hydrochloride and Hydriodide to Bornyl Chloride and Iodide. By GEORG WAGNER and W. BRICKNER (*Ber.*, 1899, 32, 2302—2325).—The authors support the conclusion of Jünger and Klages (*Abstr.*, 1896, i, 313), and of Reychler (*ibid.*), that the isobornyl chloride prepared by the action of phosphorus pentachloride on isoborneol is identical with camphene hydrochloride. They further seek to show that pinene hydrochloride is the true chloride from borneol. The so-called “bornyl chloride,” prepared by the action of phosphorus pentachloride on borneol from bornyl acetate, was found to be, for the most part, readily convertible into camphene by boiling with alcoholic potash, and therefore probably consists chiefly of isobornyl chloride (camphene hydrochloride), the borneol being converted first into camphene and then combining with a mol. of hydrogen chloride; a part of the product, however, is much more resistant to the action of alcoholic potash or of water, and it is suggested that this is probably identical with the pinene hydrochloride from turpentine oil. Riban’s chloride (*Ann. Chim. Phys.*, 1875, [v], 6, 380—383), prepared by the action of hydrogen chloride on borneol, is regarded as a mixture similar to that produced by the action of phosphorus pentachloride, but containing a larger percentage of true bornyl chloride. Attempts were also made to convert pinene hydrochloride into bornyl acetate by heating it with silver acetate and acetic acid on a water-bath during two days; the product consisted chiefly of camphene and isobornyl acetate, but did not appear to contain any bornyl acetate. The reaction proceeds much more smoothly than that employed by Marsh and Stockdale (*Trans.*, 1890, 57, 963), but it is probable that in each case the isobornyl acetate is produced by addition of acetic acid to camphene (Reychler, *Abstr.*, 1896, i, 313), and not by the direct displacement of the chlorine of the chloride by the acetoxy-radicle.

More definite results were obtained with the iodides. Pinene hydriodide (Deville, *Annalen*, 1841, 37, 176; Baeyer, *Abstr.*, 1893, i, 360)

is best prepared by the action of dry hydrogen iodide on French turpentine oil; it is a stable, heavy, colourless oil which boils at $118-119^{\circ}$ under 15 mm. pressure, solidifies in a freezing mixture, melts at -3° , and has the sp. gr. 1.4826 at $0^{\circ}/0^{\circ}$ and 1.4635 at $20^{\circ}/0^{\circ}$. When prepared from a turpentine oil of $[\alpha]_D^{37} 50'$ and washed with aqueous caustic potash, it gave $a_D -33^{\circ} 34'$ in a decimetre tube, but on heating with alcoholic potash a_D became $-32^{\circ} 40'$ after 10 hours, and $-31^{\circ} 25'$ after 40 hours treatment. It is completely freed from iodine by heating with alcoholic potash at $160-170^{\circ}$ for a short time, and at this temperature camphene is the sole product. The iodide is only slowly attacked by potassium permanganate, even on heating, but is oxidised by fuming nitric acid at -20° with separation of iodine. Silver acetate and acetic acid yield, not only camphene and the two bornyl acetates, but also dipentene and inactive terpinyl acetate; the authors regard dipentene and terpinyl acetate as the normal products of the action, and camphene and isobornyl acetate, which are produced in larger quantities at higher temperatures, are supposed to be formed by a secondary reaction.

Bornyl iodide, when prepared by moistening borneol with a little water and saturating with hydrogen iodide at the temperature of a water-bath, seems to be a mixture of two substances, one of which is readily attacked by alcoholic potash, giving an oily hydrocarbon, whilst the other is only slowly attacked and gives camphene. True *bornyl iodide*, when purified by boiling with an excess of alcoholic potash during 30 hours, closely resembles pinene hydriodide in most of its properties and reactions, but is almost inactive ($a_D = 1^{\circ} 30'$ in a decimetre tube); it boils at $118-119^{\circ}$ under 16 mm. pressure, has the sp. gr. 1.4799 at $0^{\circ}/0^{\circ}$ and 1.4617 at $20^{\circ}/0^{\circ}$, solidifies in a freezing mixture, and melts at -13° ; when treated with silver nitrate and acetic acid, it gives camphene, bornyl acetates, dipentene, and terpinyl acetate; the authors therefore regard it as identical with pinene hydriodide in all respects except its rotatory power. Isoborneol gives an oily *hydriodide* which is decomposed completely by cold alcoholic potash into camphene and potassium iodide.

The formation of bornyl chloride (pinene hydrochloride) from pinene by the action of hydrogen chloride is explained by the use of the formulæ:



The formation of terpinyl chloride by the action of hydrogen chloride has not been definitely proved, although the presence of a strongly active liquid hydrochloride has been repeatedly noticed; its production would, however, be quite analogous to that of terpinyl salts by the action of organic acids on pinene (Reychler, Abstr., 1896, i, 313).

T. M. L.

Ethereal Oil of Jasmine Flower. By ALBERT HESSE (*Ber.*, 1899, 32, 2611—2620. Compare *Abstr.*, 1899, i, 376 and 441).—Crude oil of jasmine is warmed with 10 per cent. of picric acid until a clear solution is obtained; on cooling, a considerable quantity of indole picrate separates, and the precipitation is completed by the addition of light petroleum. The amount of indole in the oil is about $2\frac{1}{2}$ per cent. The *bisulphite* compound of indole is readily produced by shaking together an ethereal solution of indole and a dilute alcoholic solution of sodium hydrogen sulphite; it separates in white, silky leaflets readily soluble in water and sparingly in methylic alcohol. Oil of jasmine also contains a small amount (about $\frac{1}{2}$ per cent.) of methyl anthranilate; this ester is detected by Erdmann and Walbaum's method (*Abstr.*, 1899, i, 620 and 621). Oil of neroli contains over 1 per cent. of this compound, and in this case it can be separated by adding the oil to a mixture of ether and concentrated sulphuric acid, when the sulphate of methyl anthranilate crystallises out; under these conditions, no precipitate is obtained with oil of jasmine.

Oil of jasmine is treated with picric acid and petroleum to remove indole, and then fractionated under diminished pressure; the fraction distilling at 100° under a pressure of 4 mm. is heated with hydroxylamine hydrochloride and alcoholic potash. The crude oxime is purified either by distilling with steam or by reprecipitation with ammonia from its solution in dilute sulphuric acid.

Jasmone, $C_{11}H_{16}O$, is obtained by hydrolysing the oxime with hot dilute sulphuric acid; the new ketone boils at $257\text{--}258^{\circ}$ under a pressure of 755 mm., and has a sp. gr. 0.945 at 15° . *Jasmone oxime*, $C_{11}H_{17}ON$, crystallises from dilute alcohol in needles, and melts at 45° . *Jasmone semicarbazone* melts at $200\text{--}204^{\circ}$; it is probably a mixture because crystallisation from alcohol separates it into a less soluble substance melting at $204\text{--}206$, and a more soluble melting at $199\text{--}201^{\circ}$. The constituents of the oil of jasmine are:

Jasmone	3.0 per cent.	linalyl acetate.....	7.5 per cent.
Indole	2.5 „	Benzyl alcohol	6.0 „
Methyl anthranilate	0.5 „	Linalool	15.5 „
Benzyl acetate	65.0 „		
			100.0

G. T. M.

Natural Resins [Ueberwallungsharze]. V. By MAX BAMBERGER and ANTON LANDSIEDL (*Monatsh.*, 1899, 20, 755—761. Compare *Abstr.*, 1899, i, 929).—The isolariciresinol, which was obtained (*loc. cit.*) by the hydrolysis of the acetyl derivatives of lariciresinol, is also formed when lariciresinol is treated with sodium in amyl alcoholic solution; it crystallises in laminæ from dilute alcohol, and melts at $95\text{--}97^{\circ}$. The *tetracetyl* derivative melts at 160° . The *dimethoxy*-derivative crystallises from alcohol in long needles melting at 165° , but the *diethoxy*-derivative is apparently identical with diethoxylariciresinol. If this isolariciresinol is boiled in benzene solution, it is transformed into an isomeric substance, $C_{19}H_{22}O_6$, which melts at $152\text{--}153^{\circ}$.

and on recrystallisation from alcohol is reconverted to isolariciresinol being probably a physical isomeride of this latter substance.

R. H. P.

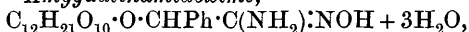
Ethereal Oils of Cresses, and the Glucosides from which they are formed. By JOHANNES GADAMER (*Arch. Pharm.*, 1899, 237, 507—521).—The method adopted was that found suitable in the case of *Tropæolum majus* (compare Abstr., 1899, i, 535).

From *Lepidium sativum* (garden cress) the same products were obtained as from *Tropæolum*, namely, benzylthiocarbimide and silver tropæolate.

From *Nasturtium officinale* (watercress), phenylethylthiocarbimide, $\text{CH}_2\text{Ph}\cdot\text{CH}\cdot\text{NCS}$, is obtained. The glucoside, *gluconasturtiin*, is a different one; on treatment with silver nitrate, it yields *silver nasturtiate*, $\text{CH}_2\text{Ph}\cdot\text{CH}_2\cdot\text{N}:\text{C}(\text{SAg})\cdot\text{O}\cdot\text{SO}_2\cdot\text{OAg} + 2\text{H}_2\text{O}$, which is soluble in ammonia in the presence of ammonium nitrate, but is precipitated by nitric acid, and is decomposed by sodium thiosulphate into phenylethylthiocarbimide and sodium sulphate. When an attempt was made to prepare an additive compound of the silver salt with ammonia, it was found that some of the silver was replaced at the same time by ammonium. It is noteworthy that the seeds do not contain an appreciable quantity of any enzyme capable of hydrolysing the glucoside.

Barbarea precox (American cress) yields the same products as *Nasturtium*.
C. F. B.

Amygdalinamidoxime. By HUGO SCHIFF (*Ber.*, 1899, 32, 2699—2702).—*Amygdalinamidoxime*,



is prepared by the action of hydroxylamine on amygdalin; it crystallises from dilute alcohol, decomposes at about 160° , has only a slightly bitter taste, and dissolves readily in water, but not in absolute alcohol, benzene or chloroform. It is lævorotatory, $[\alpha]_D - 72.2^\circ$; the mol. weight, determined from the freezing point of a solution in phenol, was 462 (calc. 490).
T. M. L.

Extractum Filicis Aethereum. By ARTHUR HAUSMANN (*Arch. Pharm.*, 1899, 237, 544—560. Compare Boehm, Abstr., 1898, i, 40).—Aspidin does not occur in extracts prepared from the roots of *Aspidium Filix mas*, Sw.; it is found in *Aspidium spinulosum*, Sw., however, and, when detected in a commercial extract, owes its presence probably to the fact that a comparatively inexpert collector has mistaken, as can easily be done, the roots of *A. spinulosum* for those of *A. Filix mas*, which are prescribed officinally. Filicic acid is present in extracts both from *A. Filix mas* and *Athyrium Filix femina*, Roth. Flavaspidic acid occurs in the extracts from all the ferns enumerated above. Albaspidin and aspidinol occur in extracts containing filicic acid, as well as in those which contain aspidin.

Poulsso's (Abstr., 1896, i, 387; 1899, i, 379) yellow and white polystichumic acids (polystichin and polystichalbin) are possibly identical with aspidin and albaspidin, and either his polystichocitrin or polystichoflavin with flavaspidic acid; in no case, however, do the analyses agree.
C. F. B.

Constitution of the Colouring Matter of Leaves: Chloroglobin. By TSVETT (*Compt. rend.*, 1899, 129, 607—610).—When plant leaves are treated with a concentrated aqueous solution of resorcinol made slightly alkaline with ammonium carbonate, the chloroplasts swell up and agglomerate, and various constituents of the cells are dissolved or liquefied, whilst the colouring matter collects in large, oily-looking drops, which coagulate at once if the resorcinol is washed out by glycerol or water. These green globules, which the author calls *chloroglobin*, are insoluble in saline solutions, but swell up in some of them (dipotassium hydrogen phosphate and potassium carbonate), and are altered by potassium carbonate; they are slowly decomposed by dilute acids, and are completely dissolved and decomposed by concentrated acids. Like many proteids, the globules absorb and retain colouring matters such as magenta, cyanin, chrysoidin, methylene-blue, and iodine-green. Chloroglobin swells up in solutions of alkali hypochlorites and is decolorised; the bleached substance gives indefinite results with the ordinary reagents for proteids. It dissolves in strong alcohol, and if this solution is agitated with benzene, a green colouring matter, which is not affected by resorcinol, passes into the latter, and a yellow substance, which is liquefied by resorcinol, remains in the alcohol.

In physico-chemical properties, chloroglobin resembles the proteids; the solubility in ether, carbon disulphide, and other organic solvents, seems to be due to the chromophoric nucleus in the molecule. The chlorophyll and carotin (xanthophyll) are probably loosely associated with the proteid nucleus.

Chloroglobin can be obtained in a very pure condition by extracting suitable leaves with strong alcohol, diluting to 20°, and collecting the very fine precipitate by filtration through porcelain. C. H. B.

Alkaloids of the Solanaceæ. By OSWALD HESSE (*Annalen*, 1899, 309, 75—94. Compare Abstr., 1892, 1498).—A specimen of atropine has been obtained from the root of *Scopolia atropoides* entirely devoid of optical activity; it melts at 115·5—116°, and the hydrobromide and hydrochloride, which are also inactive, melt at 162° and 165° respectively. The aurichloride and oxalate melt at 136° and 190—191° respectively. Gadamer (Abstr., 1897, i, 132) has also prepared inactive atropine, attributing the activity of the commercial alkaloid to the presence of hyoscyamine, and this has been found by the author to be the explanation. The rotatory power diminishes when the alkaloid is kept in the free condition, but the activity of the sulphate undergoes no change. Atropine aurichloride, contaminated with hyoscyamine aurichloride, becomes transformed into the latter in two years; the individual salt, however, undergoes no change.

The rotatory power of hyoscyamine also changes when the free alkaloid is kept, but the sulphate does not alter.

Atroscine, obtained from commercial scopolamine hydrobromide (Abstr., 1896, i, 655), melts at 82—83° when anhydrous, and is optically inactive; it crystallises with 1H₂O, then melting at 56—57°, and with 2H₂O, when it melts at 36—37°. The hydrobromide crystallises with $\frac{1}{2}$ H₂O and with 3H₂O, and melts at 181° when anhydrous. One specimen of commercial scopolamine hydrobromide examined by the

author contained 15 per cent. of atrosine hydrobromide, but all others contained 44·8—83·7 per cent. ; the new, crystallised alkaloid, obtained by E. Schmidt from hyoscyne, is stated by the author to be impure atrosine, and this is also true of Luboldt's scopolamine (*Abstr.*, 1898, i, 499).

The author emphasises the opinion already expressed (*Abstr.*, 1897, i, 132) that the name scopolamine is misleading, as the commercial hydrobromide is a mixture of hyoscyne and atrosine hydrobromides.

M. O. F.

Narcotine. By WILHELM ROSER (*Ber.*, 1899, 32, 2974. Compare *Annalen*, 1888, 247, 168).—The author points out that Frankforter and Keller (*Abstr.*, 1899, i, 781) are in error in attributing to him the statement that dimethyltolueneazammonium silver iodide is formed by the action of silver chloride on narcotine methiodide.

A. H.

α -Dinitrophenylpyridine Chloride. By EDUARD VONGERICHTEN (*Ber.*, 1899, 32, 2571—2572).—One-tenth of a per cent. of pyridine in aqueous or alcoholic solution may be detected as follows. An alcoholic solution of α -chlorodinitrobenzene is added to the liquid, and the mixture then gently warmed and shaken ; after cooling, the addition of sodium hydroxide solution produces a reddish-violet colour if pyridine is present.

A solution of α -chlorodinitrobenzene in excess of pyridine gradually deposits an additive compound, $C_{11}H_8O_4N_3Cl$, which crystallises from methyl alcohol in long, flat prisms and from acetic acid in groups of radiating needles ; it is very soluble in water or alcohol, and gives a white precipitate with silver nitrate ; the *platinichloride*, $(C_{11}H_8O_4N_3)_2PtCl_6$, and *aurichloride*, $C_{11}H_8O_4N_3AuCl_4$, form yellow precipitates. Freshly precipitated silver oxide produces in the aqueous solution no alkaline reaction, but a red, crystalline precipitate soluble in sodium hydroxide solution with the formation of a reddish-violet coloration. The addition of sodium carbonate gives a thick brown precipitate, gradually changing into a heavy, scarlet, crystalline deposit, which also gives a reddish-violet colour when dissolved in sodium hydroxide ; the same coloration is obtained by the direct addition of sodium hydroxide solution to the aqueous chloride. The red, crystalline compound has the composition $(C_{11}H_8O_4N_3)_2O$, and is the *anhydride* of the ammonium base corresponding with the chloride.

T. H. P.

Dinitrophenylpyridine Chloride. By LEOPOLD SPIEGEL (*Ber.*, 1899, 32, 2834—2836. Compare Vongerichten, preceding abstract, and Gail, *Diss. Marburg*, 1899).—The aurichloride of dinitrophenylpyridine chloride crystallises from hot water in golden flakes. The product of the action of alkalis on the chloride has the composition of an ammonium base (Gail), and not of an anhydride (Vongerichten). The chloride is oxidised by potassium permanganate and by chromic acid to dinitraniline, showing that the phenyl group is linked to the nitrogen, and not to the carbon, of the pyridine ring.

T. M. L.

Alkyl Salts of Quinolinic and Cinchomeronic Acids. By ALFRED KIRPAL (*Monatsh.*, 1899, 20, 766—778).— *β -Methyl quinolinate*

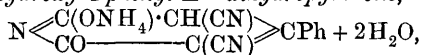
is obtained when quinolinic anhydride is boiled for 4 hours with methyl alcohol and a little acetic anhydride; it forms colourless, rhombohedral crystals from ethyl acetate melting at 123° , and its metallic salts are very similar to those of picolinic acid. When heated above its melting point, carbon dioxide is eliminated with the formation of methyl nicotinate. The corresponding β -ethyl quinolinate crystallises from benzene in colourless leaflets melting at 132° .

Monomethyl cinchomonerate, first prepared by Goldschmiedt and Strache (Abstr., 1889, 1016), melts at 172° . Its metallic salts are very similar to those of nicotinic acid, and it is probably therefore the γ -methyl cinchomeronate. Dimethyl cinchomeronate is a yellow oil which cannot be distilled. The hydrochloride melts at 141° . The author was not successful in obtaining the α -alkyl quinolines or β -alkyl cinchomeronates.

These compounds were prepared in order to test Wegscheider's rule for the esterification of dibasic acids (Abstr., 1895, ii, 310) and the results taken in conjunction with those of Goldschmiedt and Kirpal on the esterification of papaverinic acid (Abstr., 1897, i, 131) lead to the conclusion that the rule is not applicable to pyridinedicarboxylic acids.

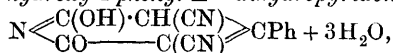
R. H. P.

Dicyanohydroxypyridones. By ICILIO GUARESCHI (*Chem. Centr.*, 1899, ii, 118—120; from *Atti Real. Accad. Torino*, 34. Compare Abstr., 1898, i, 274).—By the action of ammonia solution of sp. gr. 0.914 on a mixture of benzaldehyde (about 1 mol.), ethyl methylcyanoacetate and ethyl ethylcyanoacetate, the ammonium derivative of 3:5-dicyano-6-hydroxy-4-phenyl- $\Delta^{3,6}$ -dihydropyridone,



is obtained, together with a substance, melting at 169° , identical with Carrick's compound, $\text{CHPh}:\text{C}(\text{CN})\cdot\text{CO}_2\text{Et}$, $\text{CHPh}:\text{C}(\text{CN})\cdot\text{CONH}_2$, (Abstr., 1892, 1086). Carrick gives the melting point as 168° , and probably also obtained a mixture of this compound with the ammonium derivative of the dicyanohydroxyphenyldihydropyridone. This ammonium derivative is also obtained by the action of ammonia gas on a mixture of benzaldehyde and ethyl cyanoacetate; it crystallises from hot water in lustrous, colourless needles, is insoluble in hydrochloric acid, decomposes when heated with liberation of ammonia, forms silver, calcium, barium, &c., salts, gives a characteristic precipitate with nicotine hydrochloride, but not with coniine hydrochloride.

3:5-Dicyano-6-hydroxy-4-phenyl- $\Delta^{3,6}$ -dihydropyridone,



or dicyanophenylglutaconimide, obtained from the ammonium derivative by precipitating the silver salt and then decomposing it with hydrogen sulphide, crystallises from water in colourless needles and melts at 234 — 235° . When dissolved in water, it forms a strongly acid solution. The silver, barium, magnesium, iron, copper, and copper-ammonium derivatives are described.

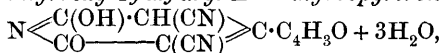
3:5-Dicyano-6-hydroxy-4-p-methoxyphenyl- $\Delta^{3,6}$ -dihydropyridone,



prepared by the action of ammonia on anisaldehyde and ethyl cyanoacetate, forms colourless crystals which are soluble in water and become coloured on exposure to the air. The corresponding *ammonium* derivative crystallises in colourless, monohydrated needles. The silver, iron, and copper-ammonium derivatives are described. A compound similar to Carrick's salt is also formed by the action of ammonia on anisaldehyde and ethyl cyanoacetate; it is only very slightly soluble in boiling water and melts at 166°.

By the action of ammonia on furfuraldehyde and ethyl cyanoacetate, the *ammonium* derivative of 3:5-dicyano-6-hydroxy-4-furfuryl- $\Delta^{3,6}$ -dihydropyridone, $\text{NH}_4\text{·C}_{11}\text{H}_4\text{O}_3\text{N}_3$, is obtained, but apparently without the formation of any bye-product; it crystallises in long, colourless, silky needles, is very soluble in boiling water, and dissolves in 550 parts of cold water.

3:5-Dicyano-6-hydroxy-4-furfuryl- $\Delta^{3,6}$ -dihydropyridone,



crystallises in long, silky needles and is soluble in warm water; the anhydrous compound melts and decomposes at 260—265°. The barium, magnesium, copper, and copper-ammonium derivatives are described. *Ethyl furfuryl- α -cyanoacrylate*, $\text{C}_4\text{H}_3\text{O·CH:C(CN)·CO}_2\text{Et}$, prepared by the action of a 1—2 per cent. solution of methylamine on furfuraldehyde and ethyl cyanoacetate, melts at 93—94°. Citral also reacts with ethyl cyanoacetate in presence of ammonia. E. W. W.

Benzoylpyridinecarboxylic Acids. By HUGO L. FULDA (*Monatsh.*, 1899, 20, 762—765).—The author has repeated Freund's experiments (Abstr., 1898, i, 43), which were not in accordance with those of Jeiteles (Abstr., 1897, i, 97), on the condensation of cinchomeronic anhydride and benzene. He finds that carbon dioxide is eliminated from the condensation product at 260°. The resulting ketone distils at 300°, melts at 63—65° and forms an oxime melting at 163—164°. The condensation product, on oxidation with acidified potassium permanganate, yields isonicotinic acid, and therefore must be 4-benzoyl-nicotinic acid. R. H. P.

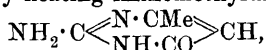
Derivatives of 4-Methylpyrimidine [4-Methyl-*m*-diazine]. By SIEGMUND GABRIEL and JAMES COLMAN (*Ber.*, 1899, 32, 2921—2935. Compare Abstr., 1899, i, 638).—The chlorine atoms of 2:6-dichloro-4-methylpyrimidine may be replaced by hydrogen, and also by other elementary and compound radicles; this substitution gives rise to the following series of pyrimidine derivatives.

2:6-Dimethoxy-4-methylpyrimidine, $\text{OMe·C} \begin{array}{c} \text{N—CMe} \\ \text{N:C(OMe)} \end{array} \text{CH}$, obtained by heating the dichloro-base with sodium methoxide and methyl alcohol, melts at 69—70°, and boils at 213° under a pressure of 763 mm.; it is a strong base, its platinichloride and aurichloride crystallise in orange-yellow and lemon-yellow needles respectively, and its picrate forms sparingly soluble, yellow leaflets.

4-Methylpyrimidine-2 : 6-dithiol, $\text{HS} \cdot \text{C} \begin{smallmatrix} \text{N}-\text{CMe} \\ \text{N}:\text{C}(\text{SH}) \end{smallmatrix} \text{CH}$, prepared by heating the dichloro-base with alcoholic potassium hydrosulphide, separates in rhombic needles when acetic acid is added to its solution in potassium hydroxide; it is almost insoluble in water and the ordinary organic solvents, and does not melt below 280° .

When the dichloro-base is treated with alcoholic ammonia, one or other of the chlorine atoms is replaced by amidogen; the separation of the two isomerides depends on their different solubilities in alcohol.

6-Chloro-2-amino-4-methylpyrimidine, $\text{NH}_2 \cdot \text{C} \begin{smallmatrix} \text{N}-\text{CMe} \\ \text{N}-\text{CCl} \end{smallmatrix} \text{CH}$, the more soluble isomeride, crystallises in colourless needles melting at $181-182^\circ$; its platinichloride, aurichloride, chromate, picrate, and ferrocyanide form a well-defined series of sparingly soluble salts; the base is also obtained by heating iminomethyluracil,

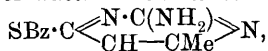


with phosphorus oxychloride, and this mode of formation serves to determine the constitution of the compound. When the base is heated with hydriodic acid and red phosphorus, iminomethyluracil is re-generated.

2-Amino-4-methylpyrimidine, $\text{NH}_2 \cdot \text{C} \begin{smallmatrix} \text{N}-\text{CMe} \\ \text{N}=\text{CH} \end{smallmatrix} \text{CH}$, produced by reducing 6-chloro-2-amino-4-methylpyrimidine with zinc dust and water, crystallises from water in glistening leaflets, and sublimes in silky needles; it melts at $159-160^\circ$, and has an odour resembling that of acetamide.

2-Amino-6-anilino-4-methylpyrimidine, $\text{NHPh} \cdot \text{C} \begin{smallmatrix} \text{CH}=\text{CMe} \\ \text{N} \cdot \text{C}(\text{NH}_2) \end{smallmatrix} \text{N}$, prepared by heating 6-chloro-2-amino-4-methylpyrimidine with aniline, crystallises from its hot aqueous or alcoholic solution in needles melting at 173° ; the platinichloride, aurichloride, chromate, and picrate are obtained as yellow, crystalline salts.

2-Amino-4-methylpyrimidine-6-thiol, $\text{NH}_2 \cdot \text{C} \begin{smallmatrix} \text{N}-\text{CMe} \\ \text{N}:\text{C}(\text{SH}) \end{smallmatrix} \text{CH}$, obtained by heating the corresponding chloropyrimidine with alcoholic potassium hydrosulphide at 100° , crystallises in yellow needles which are readily soluble in caustic alkalis or hydrochloric acid, but only sparingly so in alcohol or water. The monobenzoyl derivative,



crystallises from dilute alcohol in obliquely truncated needles, and is insoluble in alkaline solutions; it sinters at 128° and melts at $130-133^\circ$; when heated for some time above its melting point, it changes into an isomeride, which crystallises in yellow rhombohedra and melts at 189° ; this substance dissolves in solutions of caustic alkalis, and probably results from the migration of the benzoyl group from the sulphur atom to the aminic nitrogen.

2-Chloro-6-amino-4-methylpyrimidine, $\text{NH}_2 \cdot \text{C} \begin{smallmatrix} \text{N}-\text{CCl} \\ \text{CH}:\text{CMe} \end{smallmatrix} \text{N}$, the

less soluble isomeride, crystallises in colourless, truncated prisms, and melts at 215—216°; the platinichloride, aurichloride, chromate, and picrate are well-defined, yellow salts.

6-Amino-4-methylpyrimidine, $\text{NH}_2 \cdot \text{C} \begin{smallmatrix} \text{N} \text{---} \text{CH} \\ \text{CH} : \text{CMe} \end{smallmatrix} \text{N}$, prepared by reducing the preceding compound either with hydriodic acid and red phosphorus or zinc dust and water, crystallises in lustrous prisms melting at 194—195°; the aqueous solution of the base has a strongly alkaline reaction, whereas that of its 4 : 2 : 6-isomeride is neutral, the platinichloride, aurichloride, and picrate are well-defined crystalline compounds.

6-Amino-2-anilino-4-methylpyrimidine, $\text{NHPh} \cdot \text{C} \begin{smallmatrix} \text{N} \text{---} \text{CMe} \\ \text{N} : \text{C}(\text{NH}_2) \end{smallmatrix} \text{CH}$, crystallises from dilute alcohol in lustrous leaflets and melts at 118—119°.

6-Amino-4-methylpyrimidine-2-thiol, $\text{NH}_2 \cdot \text{C} \begin{smallmatrix} \text{CH} : \text{CMe} \\ \text{N} \cdot \text{C}(\text{SH}) \end{smallmatrix} \text{N}$, crystallises from hot water in iridescent, rhombic plates or flattened needles which darken on heating, but do not melt below 280°.

The hydriodide of 6-hydroxy-4-methylpyrimidine is prepared by heating 2 : 6-dichloro-4-methylpyrimidine with hydriodic acid (b. p. 127°) and red phosphorus; the base is obtained by shaking a solution of this salt with moist silver oxide; it crystallises from benzene in colourless needles melting at 149—150°.

6-Chloro-4-methylpyrimidine, $\text{CH} \begin{smallmatrix} \text{N} \cdot \text{CMe} \\ \text{N} = \text{CCl} \end{smallmatrix} \text{CH}$, produced by heating the preceding base with phosphorus oxychloride on the water-bath, melts at 38—39·5°, and boils at 173—174° under a pressure of 758 mm.; its odour resembles that of nitrobenzyl chloride. That this compound has the constitution indicated by the formula is shown by the fact that it yields 6-amino-4-methylpyrimidine when heated at 100° with alcoholic ammonia.

6-Anilino-4-methylpyrimidine, $\text{NHPh} \cdot \text{C} \begin{smallmatrix} \text{N} \text{---} \text{CH} \\ \text{CH} : \text{CMe} \end{smallmatrix} \text{N}$, obtained by heating aniline and the preceding chloro-base at 100°, crystallises from water in felted needles melting at 146°; its platinichloride forms felted, yellow needles.

4-Methylpyrimidine-6-thiol, prepared by heating 6-chloro-4-methylpyrimidine with an alcoholic solution of potassium hydrosulphide, crystallises from boiling water in obliquely truncated needles or rhombic plates; it melts and decomposes at 255°, and is readily soluble in caustic alkalis.

The disulphide, $(\text{C}_5\text{H}_5\text{N}_2)_2\text{S}_2$, formed by oxidising the sodium derivative of the preceding thiol-base with a solution of iodine in potassium iodide, separates from light petroleum in granular crystals melting at 105—107°.

6-Iodo-4-methylpyrimidine, $\text{CH} \begin{smallmatrix} \text{N} \cdot \text{CMe} \\ \text{N} = \text{CI} \end{smallmatrix} \text{CH}$, is obtained as hydriodide by the action of fuming hydriodic acid on 2 : 6-dichloro-4-methylpyrimidine (*loc. cit.*), melts at 20°, and yields 6-anilino-4-methylpyrimidine on heating at 100° with aniline. When the

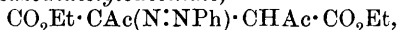
2:6:4- or the 6:2:4-chloroaminomethylpyrimidine is heated at 195° with carbamide, a *compound* is obtained having a composition corresponding with that required by the formula $C_8H_{11}O_3N_7$.

The *base*, $C_{10}H_6O_2N_6$, produced by adding 4-methylpyrimidine to excess of fuming nitric acid, crystallises from water in glistening rhombohedra or rhombic plates, and melts at 134°; the *nitrate* crystallises in thick, yellow prisms melting at 157°; and the *platinichloride* forms orange-yellow needles.

G. T. M.

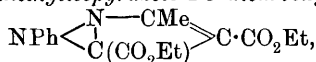
Preparation of Isopyrazole Derivatives from Diethyl Benzeneazodiacetylsuccinate. By CARL BÜLOW and ALFRED SCHLESINGER (*Ber.*, 1899, 32, 2880—2891).—The elimination of an acetyl group from α -substituted ethyl acetoacetates, $CHRAc \cdot CO_2Et$, is a necessary step in the formation of hydrazones, $N_2HPh \cdot CR \cdot CO_2Et$, by the action of diazo- and isodiazo-compounds on these esters (V. Meyer, *Abstr.*, 1888, 366) and the results of previous investigators indicate that the reaction invariably takes place in this sense (Japp and Klingemann, *Trans.*, 1888, 53, 332, and Bischler, *Abstr.*, 1893, i, 44 and 610). Benzenediazonium chloride, however, combines with diethyl diacetylsuccinate without displacing an acetyl group.

Diethyl benzeneazodiacetylsuccinate,



is obtained as a pale yellow precipitate on adding sodium acetate to a dilute alcoholic solution containing benzenediazonium chloride and the diketonic form of diethyl diacetylsuccinate; it crystallises in lustrous, yellow leaflets melting at 108° and is soluble in the ordinary organic solvents. With concentrated sulphuric acid, it yields a clear yellow solution, whilst potassium permanganate or dichromate develops a violet coloration. Although the insolubility of the compound in cold, dilute alkalis seems to indicate that it has the diketonic constitution, yet the fact that it is not acted on by excess of the diazonium salt tends to show that it possesses the alternative keto-enolic formula, $CO_2Et \cdot CAc(N:NPh) \cdot C(CO_2Et) \cdot CMe \cdot OH$.

Diethyl 1-phenyl-3-methylisopyrazole-4-5-dicarboxylate,



produced by boiling the preceding compound with water for 10 hours, crystallises from dilute alcohol in almost colourless, transparent, monoclinic plates [$a:b:c = 0.6072:1:0.9663$; $\beta = 112^\circ 37'$] and melts at 51.5°; it is readily soluble in the ordinary organic solvents, but not in water. In small quantities, it may be distilled without decomposition; it is not attacked by concentrated sulphuric acid, and when reduced in alcoholic solution gives Knorr's pyrazoline reaction.

1-Phenyl-3-methylisopyrazole-4:5-dicarboxylic acid, obtained either by hydrolysing the preceding ester with acids or alkalis or by boiling the original azo-compound with dilute caustic soda solution, melts at 247°; its isomeride, 1-phenyl-5-methylisopyrazole-3:4-dicarboxylic acid, melts at 198° (Knorr and Laubmann, *Abstr.*, 1899, 409). The *silver salt*, $AgC_{12}H_9N_2O_4$, is obtained by treating the *acid ammonium salt* with silver nitrate; the acid is shown to be dibasic by titrating with standard caustic alkali in presence of phenolphthalein.

1-Phenyl-3-methylisopyrazole, $\text{NPh} \begin{array}{c} \text{N}-\text{CMe} \\ \diagup \quad \diagdown \\ \text{CH} \cdot \text{CH} \end{array}$, is obtained as an oil

when the preceding compound is heated above its melting point; it boils at $255-265^\circ$ under a pressure of 744 mm. and possesses an odour like that of quinoline. The *methiodide* melts at 287° , the *platinichloride* crystallises in yellow plates with ragged edges and melts at 198° . G. T. M.

Double Chloride of Copper and Antipyrine. By M. C. SCHUYTEN (*Chem. Centr.*, 1899, ii, 37; from *Bull. Acad. roy. Belg.*, [iii] 37, 140—142).—The salicylate of copper and antipyrine (compare Abstr., 1899, i, 306) contains only one mol. of base. The chloride of copper and antipyrine, $\text{CuCl}_2(\text{C}_{11}\text{H}_{12}\text{N}_2\text{O})_2$, prepared by mixing solutions of cupric chloride and antipyrine, crystallises in ruby needles, melts at 145° and dissolves in water, forming a greenish acid solution which gives the characteristic reactions of copper and antipyrine. E. W. W.

Metallic Benzopyrines. By M. C. SCHUYTEN (*Chem. Centr.*, 1899, ii, 38; from *Bull. Acad. roy. Belg.*, [iii], 37, 126—134).—The benzoates of iron, aluminium, copper, and uranium take up antipyrine in the largest quantities and retain it most stubbornly, but they do not form compounds of constant composition. Similarly, benzoic acid and the benzoates of magnesium, chromium, manganese, cobalt, nickel, zinc, silver, cadmium, gold, mercury, and lead form only more or less stable mixtures with antipyrine.

The properties and behaviour of the various substances obtained are described in the original paper. E. W. W.

Constitution of Metallic Salipyrines. By M. C. SCHUYTEN (*Chem. Centr.*, 1899, ii, 38; from *Bull. Acad. roy. Belg.*, [iii], 37, 135—139).—The capability of metallic salicylates of forming double compounds with antipyrine must be due to the presence of a hydroxyl group, since benzoates do not form such compounds. This property, however, is easily destroyed, as, for instance, by the presence of the groups characteristic of anhydrides, for the phthaleins do not combine with antipyrine. The salipyrines are divided into the following classes: (1) those of the type of the iron compound; (2) the magnesium, manganese, cobalt, nickel, zinc, and cadmium compounds; (3) the copper and lead compounds and (4) the aluminium, chromium, silver, gold, mercury and uranium compounds, which cannot be prepared by the usual methods. Constitutional formulæ for the compounds of the first three classes are given in the original paper. E. W. W.

Formation of Ring Compounds by Elimination of Aromatic Nitro-groups. By ALFRED WERNER and TH. HERBERGER (*Ber.*, 1899, 32, 2686—2696. Compare V. Meyer, Abstr., 1889, 516; Turpin, Trans., 1891, 59, 714—725; and Kehrman and Messinger, Abstr., 1894,

i, 55).—6-Nitro-3-phenyl-2:4- Δ^2 -benzazoxazine, $\text{NO}_2 \cdot \text{C}_6\text{H}_5 \begin{array}{c} \text{O}-\text{N} \\ \diagup \quad \diagdown \\ \text{NH} \cdot \text{CPh} \end{array}$, prepared by the action of alcoholic potash on 2:4-dinitrophenylbenzenyl-

aminoxime (Werner, Abstr., 1894, i, 461), crystallises from chloroform in reddish-brown, pleochroic prisms, or from concentrated solution in bundles of yellow prisms or plates; the two modifications have the same composition, and often separate together from solution, and as the labile hydrogen atom is known to wander from the 4- to the 2-position, it is suggested that these may represent the two isomeric forms. The substance becomes dark red at 168° and melts at 173°; like all members of the series containing the NH group, it gives a blue solution with alcoholic potash (*Ber.*, 1886, 19, 1669).

Benzenylanilinoxime (Müller, Abstr., 1886, 875) was prepared by the action of aniline on benzhydroximic chloride. The 2:4-dinitrophenyl ether, $\text{NHPh} \cdot \text{CPh} : \text{N} \cdot \text{O} \cdot \text{C}_6\text{H}_3(\text{NO}_2)_2$, prepared by the action of sodium ethoxide on an alcoholic solution of benzenylanilinoxime and dinitrochlorobenzene, crystallises from hot alcohol in orange-yellow prisms and melts at 150°; a colourless substance is also produced which crystallises from hot alcohol in long, quadratic prisms, melts at 173°, and has the composition of a nitrodiethoxybenzene, $\text{NO}_2 \cdot \text{C}_6\text{H}_3(\text{OEt})_2$.

6-Nitro-3:4-diphenylbenzazoxazine, $\text{NO}_2 \cdot \text{C}_6\text{H}_3 \begin{smallmatrix} \text{O} \text{---} \text{N} \\ | \\ \text{NPh} \cdot \text{CPh} \end{smallmatrix}$, crystallises from chloroform in well-formed, amber-yellow, rhombic prisms, and melts at 168°; only one modification was observed.

Dinitrophenyl-p-tolensylaminioxime, $\text{C}_6\text{H}_4\text{Me} \cdot \text{C}(\text{NH}_2) : \text{N} \cdot \text{O} \cdot \text{C}_6\text{H}_3(\text{NO}_2)_2$, crystallises from alcohol in sulphur-yellow, hexagonal prisms and melts

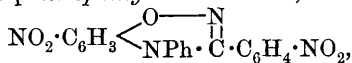
at 174°. 6-Nitro-3-p-tolylbenzazoxazine, $\text{NO}_2 \cdot \text{C}_6\text{H}_3 \begin{smallmatrix} \text{O} \text{---} \text{N} \\ | \\ \text{NH} \cdot \text{C} \cdot \text{C}_6\text{H}_4\text{Me} \end{smallmatrix}$, crystallises from chloroform in dark orange-red, rhombic prisms or tablets, melts at 185°, and is readily soluble in chloroform or acetone. The carbanilide crystallises from alcohol in long, sulphur-yellow, rhombic needles, and melts at 270°.

2:4-Dinitrophenyl-p-nitrobenzenylanilinoxime,
 $\text{NO}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{C}(\text{NH}_2) : \text{N} \cdot \text{O} \cdot \text{C}_6\text{H}_3(\text{NO}_2)_2$,
 crystallises from alcohol in pale yellow needles and melts at 240°.

6-Nitro-3-p-nitrophenylbenzazoxazine, $\text{NO}_2 \cdot \text{C}_6\text{H}_4 \begin{smallmatrix} \text{O} \text{---} \text{N} \\ | \\ \text{NH} \cdot \text{C} \cdot \text{C}_6\text{H}_4 \cdot \text{NO}_2 \end{smallmatrix}$, crystallises from acetone in dark-red needles, melts at 126°, and dissolves slightly in ether or alcohol.

p-Nitrobenzenylanilinoxime, $\text{NO}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{C}(\text{NHPh}) : \text{NOH}$, crystallises from alcohol in lemon-yellow needles and melts at 183°. The 2:4-dinitrophenyl ether crystallises from alcohol in dark orange-red prisms and melts at 177°.

6-Nitro-4-phenyl-3-p-nitrophenylbenzazoxazine,



crystallises from chloroform in orange-yellow, hexagonal prisms and melts at 182°.

Dinitrophenyl-m-nitrobenzenylanilinoxime crystallises from alcohol in long, sulphur-yellow prisms and melts at 222°. 6-Nitro-3-m-nitrophenylbenzazoxazine crystallises from acetone in orange-red, rhombic prisms and flakes, melts at 118°, is insoluble in alcohol, but dissolves in alcoholic potash, forming a dark blue solution.

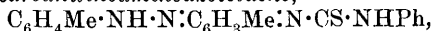
m-Nitrobenzenylanilinoxime, prepared by the action of aniline on *m*-nitrobenzhydroxamic chloride, crystallises from alcohol in yellow needles and melts at 158°; the 2:4-dinitrophenyl ether crystallises from acetic acid in lemon-yellow flakes, melts at 162°, and is soluble in acetone.

6-Nitro-4-phenyl-3-*m*-nitrophenylbenzazoxazine crystallises from chloroform in yellow flakes, dissolves slightly in alcohol or ether, and melts at 189°.

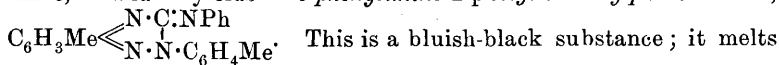
Benzylbenzenylamininoxime, $\text{NOH}\cdot\text{CPh}\cdot\text{NH}\cdot\text{CH}_2\text{Ph}$, crystallises from alcohol in white flakes, melts at 120°, and dissolves readily in ether.

The 2:4-dinitrophenyl ether crystallises from alcohol in bunches of long, yellow needles, melts at 130°, and dissolves in ether or chloroform. 6-Nitro-3-phenyl-4-benzylbenzazoxazine crystallises from alcohol in long, greenish-yellow needles, melts at 136°, and dissolves readily in alcohol, chloroform, or light petroleum. T. M. L.

Triazines from *o*-Aminoazo-compounds. By MAX BUSCH (with LUDWIG HARTMANN; *Ber.*, 1899, 32, 2959—2972).—Carbanilino-aminoazotoluene (Goldschmidt and Rosell, *Abstr.*, 1890, 616) could not be made to undergo internal condensation with elimination of water, but thiocarbanilinoaminoazotoluene,

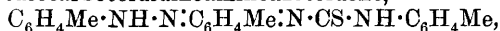


(which is formed from phenylthiocarbimide and *o*-aminoazotoluene in concentrated alcoholic solution, is yellow, and melts at 149°), loses hydrogen sulphide when treated in benzene solution with mercuric oxide, and yields 3-phenylimino-2-*p*-tolyl-7-methylphenotriazine,



at 127.5°, and is basic in character; the brownish-red *hydrochloride*, with $(\text{C}_{21}\text{H}_{18}\text{N}_4)_2\cdot 3\text{HCl}$, melting at 98°, brown *platinichloride*, melting above 260°, and dark blue *picrate*, melting at 204°, were analysed. The triazine is converted by acid reducing agents, best in benzene solution with hydrogen sulphide, to 3-phenylimino-2-*p*-tolyl-7-methyl-dihydrophenotriazine, $\text{C}_6\text{H}_3\text{Me} \begin{array}{c} \text{NH}\cdot\text{C}:\text{NPh} \\ \text{NH}\cdot\text{N}\cdot\text{C}_6\text{H}_4\text{Me} \end{array}$; this is yellowish, melts at 141°, and oxidises readily in the air.

A similar series of compounds was prepared from *p*-tolylthiocarbimide; thiocarbotoluidinoaminoazotoluene,



is brownish-yellow, and melts at 155°. 3-Tolylimino-2-*p*-tolyl-7-methylphenotriazine is bluish-black, and melts at 147°, the *hydrochloride*, with $1\frac{1}{2}\text{HCl}$, is dark claret, and melts at 103°, the *platinichloride* is dark red, and the *picrate*, melting at 216°, is deep violet-blue; the corresponding dihydrotriazine is yellowish, and melts at 166—168°.

2-Tolylketo-7-methylphenotriazine, $\text{C}_6\text{H}_4\text{Me} \begin{array}{c} \text{N}\cdot\text{CO} \\ \text{N}\cdot\text{N}\cdot\text{C}_6\text{H}_4\text{Me} \end{array}$, is formed from *o*-aminoazotoluene and carbonyl chloride in benzene-toluene solution; it is red, melts at 168°, and forms salts which are decomposed by water; the dark claret *hydrochloride* melts at 154°. Alcoholic potash converts it into yellow ethyl *o*-tolueneazotolylcarb-

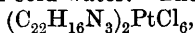
amate, $C_6H_4Me \cdot NH \cdot N : C_6H_4Me \cdot N \cdot CO_2Et$ (also formed from *o*-aminoazotoluene and ethyl chloroformate in the presence of pyridine and in benzene solution), which melts at 94° and has no basic properties; alcoholic ammonia converts it into the corresponding yellow *carbamide* melting at 207° , and aniline into the anilide (carbanilinoaminoazotoluene, *loc. cit.*). Acid-reducing agents convert it into the *di-hydroketotriazine*, which melts at 146° , and oxidises readily in the air; zinc powder and acetic anhydride convert it into the *acetyl* derivative of this, $C_6H_4Me \cdot \begin{matrix} NH-CO \\ | \\ NAc \cdot N \cdot C_6H_4Me \end{matrix}$ which melts at 190° and is stable in the air.

2-Phenylketonaphthatriazine, prepared by Goldschmidt and Rosell (*loc. cit.*) from benzeneazo- β -naphthylamine and phenylcarbimide, is also formed from the benzeneazo- β -naphthylamine and carbonyl chloride. With alcoholic potash, it yields benzeneazo- β -naphthylamine, not a carbamate. The latter, *ethyl benzeneazo- β -naphthylcarbamate*, can be prepared, though with some difficulty, from benzeneazo- β -naphthylamine and ethyl chloroformate; it is orange-red, melts at 110° , and is converted by cold alcoholic potash into the ketotriazine.

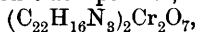
C. F. B.

The Eighth and Ninth Isomerides of Rosinduline. By FRIEDRICH KEHRMANN and P. FILATOFF (*Ber.*, 1899, 32, 2627—2633. Compare Abstr., 1898, i, 154, 155; 1899, i, 238, 525).—When well dried phenylnaphthaphenazonium nitrate (Abstr., 1897, i, 172) is added to about 5 times its weight of the strongest nitric acid, cooled to 0° , the solution allowed to remain at this temperature for 2—3 hours and then diluted with ice, a more or less crystalline precipitate, consisting of a mixture of two isomeric *mononitro*-derivatives, is deposited. These may be separated by the aid of cold alcohol, in which one is only sparingly soluble.

The sparingly soluble nitrate dissolves in warm alcohol, yielding a lemon-yellow, non-fluorescent solution, which, when boiled, undergoes decomposition; when its alcoholic solution is reduced with stannous chloride and concentrated hydrochloric acid and then allowed to cool, crystals of the stannochloride of the leuco-compound are deposited. This is converted into *aminophenylnaphthaphenazonium chloride* (*rosinduline* No. 8) by boiling with 25 per cent. alcohol, and aspirating air through the boiling solution, filtering and treating the residue in exactly the same manner until the residue consists of pale grey tin hydroxide. When recrystallised from alcohol, it forms short, glistening, violet prisms with a metallic lustre, and still retains $1H_2O$ at 110° . Its aqueous solution has a greenish-blue, its alcoholic solution, a pure green, colour, and its solution in sulphuric acid is golden-yellow, but none of these exhibit fluorescence. The *nitrate*, $C_{22}H_{16}N_3 \cdot NO_3$, crystallises from alcohol in small, violet, glistening prisms sparingly soluble in cold water. The *platinichloride*,



is a sparingly soluble, green-black powder, and the *dichromate*,



a dark-green, crystalline powder insoluble in water.

When the readily soluble nitro-derivative is reduced and the product treated as above, a chloride (*isorosinduline* No. 8) is obtained; it crystallises from alcohol in long, violet prisms, dissolves in water, giving a deep-blue solution, in alcohol yielding a greenish-blue solution, and in sulphuric acid to a blood-red solution. The *platinichloride*, $(C_{22}H_{16}N_3)_2PtCl_6$, is a dark blue, and the *dichromate* a green, crystalline precipitate.

The constitutions of the two isorosindulines have not been established.

J. J. S.

Nitro- and Amino-flavindulines. By FRIEDRICH KEHRMANN and ZENAIDE KIKINE (*Ber.*, 1899, 32, 2633—2637).—When phenanthraquinone is treated with fuming nitric acid, it yields various nitro-derivatives (compare Anschütz and Schultz, this Journal, 1877, i, 210; Schmidt, *Abstr.*, 1879, 941; Strasburger, *ibid.*, 1884, 328; Schultz, *ibid.*, 1880, 814). The authors have isolated a *mononitro*-derivative melting at 161—162°, and a *dinitro*-derivative, melting at 279°, which appears to be identical with the compound described by Graebe (*Abstr.*, 1873, 895); no mononitro-compound melting at 257° (compare Anschütz) could be found.

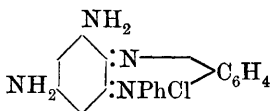
Nitroflavinduline, $NO_2 \cdot C_{14}H_7 \begin{smallmatrix} \text{N} \\ \text{NPhCl} \end{smallmatrix} > C_6H_4$, is obtained when the mononitro-derivative melting at 161° is suspended in glacial acetic acid, mixed with the requisite amount of phenyl-*o*-phenylenediamine hydrochloride, and allowed to remain at the ordinary temperature until complete solution ensues, an operation requiring several days. It forms thick, amber-yellow prisms, readily soluble in water or alcohol, but insoluble in ether, its solutions being golden-yellow in colour and non-fluorescent. The *platinichloride*, $(C_{26}H_{16}O_2N_3)_2PtCl_6$, forms a reddish-yellow, crystalline precipitate practically insoluble in water, and the *dichromate* a flocculent precipitate of the same colour. When reduced with stannous chloride and hydrochloric acid, the nitro-compound is converted into the sparingly soluble stannochloride of the leuco-derivative of aminoflavinduline; the latter is then oxidised with ferric chloride, dissolved in water, treated with an excess of sodium acetate, filtered, and treated with solid sodium bromide, when *amino-flavinduline bromide*, $C_{26}H_{18}N_3Br$, separates in the form of dark green needles readily soluble in water and in concentrated sulphuric acid; the *dichromate*, $(C_{26}H_{18}N_3)_2Cr_2O_7$, forms a green, insoluble precipitate.

2:7-Dinitroflavinduline, $C_{14}H_6(NO_2)_2 \begin{smallmatrix} \text{N} \\ \text{NPhCl} \end{smallmatrix} > C_6H_4$, obtained when dinitrophenanthraquinone is condensed with *o*-aminodiphenylamine hydrochloride, crystallises from acetic acid in small, lemon-yellow prisms, is readily soluble in cold water, but only sparingly in cold alcohol. *2:7-Diamino-flavinduline bromide*, $C_{26}H_{19}N_4Br$, crystallises in short, blackish-green prisms moderately soluble in water; the *dichromate* forms a dark green powder insoluble in water. J. J. S.

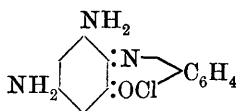
Constitution of Oxazine Dyes, and Quadrivalent Oxygen. By FRIEDRICH KEHRMANN (*Ber.*, 1899, 32, 2601—2611). [With KRAMER.]—*Isophenosaffranine chloride*, $C_{18}H_{15}N_4Cl$, is obtained by reducing 1:3-dinitro-5-phenyldihydrophenazine (*Abstr.*, 1893, i, 55) with

stannous chloride, oxidising a dilute acetic acid solution of the leuco-base so produced with atmospheric oxygen, and precipitating the dye with sodium chloride; it crystallises from water in greenish-black needles having a metallic lustre; its solution in alcohol or water is bluish-green. When dissolved in concentrated sulphuric acid, an orange coloration is produced; on diluting this solution with water, it becomes red, and then contains the diacid salt; on further dilution, or partial neutralisation, the green tint of the monacid salt is developed. The base is not liberated from its monacid salts by sodium carbonate or ammonia, and only partially by caustic alkalis. The *nitrate* crystallises in greenish-black, sparingly soluble needles. The *platinichloride* and the dichromate are obtained as green precipitates.

The colour base obtained by replacing the group :NPh· in isosaffranine by oxygen or sulphur closely resembles this compound in chemical and physical properties; this resemblance, however, is not indicated by the formulæ commonly given to hydrochlorides of oxazines and thiazines, the oxy- and thio-analogues of isosaffranine being represented as paraquinonoid derivatives, whereas isosaffranine chloride must be an orthoquinonoid substance. If, however, it is assumed that oxygen and sulphur are quadrivalent in these salts (compare Collie and Tickle, *Trans.*, 1899, **75**, 710), then it becomes possible to give constitutional formulæ to these substances analogous to that of the nearly related isosaffranine chloride, as follows:



Isosaffranine chloride.

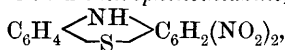


Diaminophenazoxonium chloride.

[With P. THOMAS].—*Diaminophenoxazine*, $C_{12}H_{11}ON_3$, is obtained in the form of its stannochloride by reducing dinitrophenoxazine (Turpin, *Trans.*, 1891, **59**, 714) with stannous chloride.

Diaminophenazoxonium bromide, $C_{12}H_{10}ON_2Br$, prepared by oxidising an acetic acid solution of the preceding base with a current of air and then adding sodium bromide, crystallises from water in dull black leaflets; the aqueous solution has a green colour and a bitter taste. The base is liberated by caustic alkalis and sodium carbonate, but not by ammonium carbonate. The hydrobromide, when dissolved in concentrated sulphuric acid, gives a dark red solution which becomes brownish-yellow on dilution with water. The basic character of the compound persists even when the two amino-groups are acetylated.

[With L. SCHILD].—3:5-*Dinitrophenothiazine*,



produced by heating picrylaminothiophenol with alcoholic sodium hydroxide, crystallises from alcohol in dark, reddish-brown needles with a green reflex. With alcoholic alkalis, it yields unstable bluish-violet salts which are decomposed by water; its solution in concentrated sulphuric acid is brownish-red.

3:5-*Diaminophenothiazine* is obtained by reducing the preceding compound with stannous chloride, and is identified by means of its

diacetyl derivative; the latter is produced by heating the stannochloride with acetic anhydride and dry sodium acetate; it crystallises from alcohol or glacial acetic acid in greenish-yellow needles insoluble in water.

3:5-Diaminophenazothionium chloride, $C_{12}H_{10}N_2SCl + H_2O$, prepared by oxidising diaminophenothiazine with atmospheric oxygen or ferric chloride, crystallises from water in reddish-brown needles with green reflex. The *platinichloride* and *dichromate* are dark green precipitates. The base is liberated from its salts by caustic alkalis, but not by carbonates; on the other hand, it combines directly with carbon dioxide, and decomposes ammonium carbonate.

Alcoholic solutions of the bromide of the azoxonium base, and the chlorides of the azothionium base and isosaffranine have very similar absorption spectra, the blue and violet portions of the spectrum being completely obscured in each case.

G. T. M.

Aminouracil. By ROBERT BEHREND and RICHARD GRÜNWARD (*Annalen*, 1899, **309**, 254—260).—Aminouracil, $C_4N_2H_3O_2 \cdot NH_2$ (Behrend, *Annalen*, 1885, **229**, 38), is best obtained by reducing nitrouracil with ammonia and zinc dust. The *sodium* and *potassium* derivatives were prepared; the *sulphate* forms needles containing $5H_2O$, and the *nitrate* crystallises in lustrous leaflets with $1H_2O$. The *picrate* melts at $147-148^\circ$; the *acetyl* derivative sublimes without decomposing, and the *benzoyl* derivative crystallises from alcohol in leaflets melting at $283-287^\circ$.

M. O. F.

Isomerism of the Methyluric Acids. By EMIL FISCHER and FRIEDRICH ACH (*Ber.*, 1899, **32**, 2721—2749).—The usual formula for uric acid accounts for the existence of only four monomethyl derivatives; a fifth, however, has been obtained by von Loeben (*Abstr.*, 1898, **74**, 128) and in this paper is given an account of a sixth isomeride.

ζ -Methyluric acid, $C_6H_6O_3N_4$, is obtained by heating a solution of potassium urate in dilute acetic acid with methyl iodide or chloride at 100° . It separates from boiling water in the form of short, microscopic prisms or rectangular tablets containing $1H_2O$. It dissolves in 600 parts of boiling water. When heated, it chars without melting. It gives the murexide test on treatment with nitric acid and reduces ammoniacal silver nitrate solution.

The *dipotassium* salt of the ζ -acid is more soluble in dilute alcohol than that of uric acid. A *sodium hydrogen* salt, $C_6H_5O_3N_4Na + 4H_2O$, forms spherical aggregates of slender needles. The *barium hydrogen* salt, with $4H_2O$, forms aggregates of needles or prisms, and the *calcium hydrogen* salt, with $2H_2O$, forms beautiful, shining needles.

When ζ -methyluric acid is oxidised with potassium chlorate and hydrochloric acid, it yields methylalloxan.

The methylation of ζ -uric acid leads to the formation of products which differ with the mode of treatment. With excess of alkali and methyl iodide, hydroxycaffeine and tetramethyluric acid are produced at $35-40^\circ$, and hydroxycaffeine and 1:3-dimethyluric acid at $0-20^\circ$.

7-Chloro-2 : 5-dioxy-4-methylpurine, $\begin{array}{c} \text{N}:\text{CCl}-\text{C}\cdot\text{NH} \\ | \quad | \\ \text{CO}\cdot\text{NMe}\cdot\text{C}\cdot\text{NH} \end{array} > \text{CO}$, formed when ζ -methyluric acid is heated with phosphorus oxychloride at 130° , crystallises in glistening, colourless needles; it does not melt, but slowly decomposes above 300° . It dissolves in 105—110 parts of boiling water, and is sparingly soluble in acetone, chloroform, or ethyl acetate. It has fairly powerful acidic properties; the *potassium*, *sodium*, *ammonium*, and *barium* derivatives are described. It is only feebly basic.

2 : 5-Dioxy-4-methylpurine, $\begin{array}{c} \text{N}:\text{CH}-\text{C}\cdot\text{NH} \\ | \quad | \\ \text{CO}\cdot\text{NMe}\cdot\text{C}\cdot\text{NH} \end{array} > \text{CO}$, obtained by heating 7-chloro-2 : 5-dioxy-4-methylpurine with strong hydriodic acid and phosphonium iodide on the water-bath, separates from boiling water in clear, compact prisms or tablets containing $\frac{1}{2}\text{H}_2\text{O}$. The base decomposes without melting at a high temperature, dissolves in 35—40 parts of water, and is readily soluble in dilute acids, ammonia, or alkalis; the *hydrochloride* crystallises in compact, colourless prisms. The constitution of the substance was ascertained by exhaustive methylation, when a considerable quantity of 2 : 5-dioxy-1 : 3 : 4-trimethylpurine was produced.

7-Amino-2 : 5-dioxy-4-methylpurine, $\begin{array}{c} \text{N}:\text{C}(\text{NH}_2)\cdot\text{C}\cdot\text{NH} \\ | \quad | \\ \text{CO}\cdot\text{NMe}\cdot\text{C}\cdot\text{NH} \end{array} > \text{CO}$, produced when 7-chloro-2 : 5-dioxy-4-methylpurine is heated at $135\text{--}140^\circ$ with 18 per cent. ammonia, forms a white, crystalline powder which is very sparingly soluble in water and decomposes without melting when heated. The *hydrochloride* forms aggregates of white needles, and the *sulphate*, slender needles or long, acicular crystals which frequently form spherical aggregates. A solution of the base in hydrochloric acid gives a precipitate of slender, yellow, flexible needles on addition of auric chloride. The *potassium* and *sodium* derivatives were prepared. The base is at once destroyed by nitric acid and the solution exhibits the murexide reaction in a very marked manner.

When 7-chloro-2 : 5-dioxy-4-methylpurine is heated with dilute soda and methyl iodide, the halogen is eliminated and hydroxycaffeine is formed; in one instance, a substance was obtained having the composition of an iododioxymethylpurine, which yielded trimethyluric acid on treatment with acids. Chloro-4-methylxanthine is formed as a bye-product in the reaction between ζ -methyluric acid and phosphorus oxychloride, and may be prepared by heating the foregoing chlorodioxymethylpurine with phosphorus oxychloride at $140\text{--}145^\circ$ for $2\frac{1}{2}$ hours.

δ -Methyluric acid resembles the ζ -derivative in general properties, solubility, hydration, behaviour on heating, and the appearance and solubility of its potassium salt, but differs markedly from it in its behaviour towards phosphorus oxychloride, which attacks it only with great difficulty at 130° , yielding, however, a small quantity of chloro-4-methylxanthine; the latter is more readily produced at $140\text{--}145^\circ$. δ -Methyluric acid also yields tetramethyluric acid when heated with methyl iodide and soda at 100° .

ζ -Methyluric acid may be converted into the δ -derivative, iether (1) by treatment with phosphorus oxychloride and hydrolysis of the

resulting chloropurine with 5 per cent. hydrochloric acid, when a mixture of the two isomeric acids is obtained, whence the ζ -derivative may be removed by the use of phosphorus oxychloride; (2) by heating with hydrochloric acid for 9 hours on the water-bath; (3) by heating with normal potassium hydroxide in closed tubes at 100° , when a fairly complete conversion is effected.

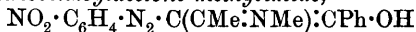
A partial conversion of the δ - into the ζ -derivative has been accomplished by heating it at 100° with hydrochloric acid in a closed tube for 18 hours.

It is found that on oxidising the various methyluric acids with potassium permanganate or lead peroxide, the α -, ζ -, δ -, and 3-methyl derivatives yield the same methylallantoin, whilst the 1- and 6-methyluric acids afford a second; these products the authors distinguish by the prefixes α - and β - respectively.

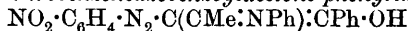
α -Methylallantoin melts and decomposes at 248 — 249° (corr. 255 — 259° [not 225° as stated by Hill (this Journal, 1876, 30, 509)]). β -Methylallantoin melts, when rapidly heated, at 219 — 221° (corr. 225 — 227°), dissolves readily in hot water, and crystallises in large, colourless prisms containing $1\text{H}_2\text{O}$; on reduction with hydriodic acid, it yields a methylhydantoin probably identical with that obtained by methylating hydantoin. A. L.

Inactive *b-p*-Nitranilineazobenzoylacetone [*p*-Nitrobenzeneazobenzoylacetone] and its Derivatives. By CARL BÜLOW (*Ber.*, 1899, 32, 2637—2649. Compare Abstr., 1899, i, 271).—*Inact-p-nitrobenzeneazobenzoylacetone*, $\text{NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{N}:\text{N}\cdot\text{CHAcBz}$, is obtained when an aqueous solution of *p*-nitroisodiazobenzenesodium (nitrosamine-red of the Badische Anilin- und Soda-Fabrik) and of sodium carbonate is mixed with a cold alcoholic solution of benzoylacetone, and the mixture allowed to remain for 12 hours. It crystallises from hot alcohol or acetic acid in brownish-yellow, jagged plates melting at 141 — 142° , and dissolves in acetone, benzene, or toluene; it is also soluble in dilute alkalis, and is reprecipitated on the addition of acids. It is not decomposed by boiling with ammonium hydroxide, or by adding potassium dichromate, ferric chloride, or amyl nitrite to its solution in cold concentrated sulphuric acid. The *potassium* derivative, $\text{NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{N}:\text{N}\cdot\text{CKAcBz}$, forms large, reddish-violet, glistening plates.

p-Nitrobenzeneazobenzoylacetone methylimide,



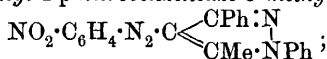
or $\text{NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{N}_2\cdot\text{C}(\text{CPh}:\text{NMe})\text{:CMe}\cdot\text{OH}$, is slowly deposited as orange needles melting at 155° when an excess of aqueous methylamine solution is added to a warm, alcoholic solution of the condensation product. When the condensation product is boiled for an hour with an excess of aniline, then allowed to remain for 12 hours, and alcohol added, *p*-nitrobenzeneazobenzoylacetone phenylimide,



or $\text{NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{N}_2\cdot\text{C}(\text{CPh}:\text{NPh})\text{:CMe}\cdot\text{OH}$, separates slowly in the form of long, orange-brown needles melting at 146° . It dissolves in cold acids, but on boiling, decomposition ensues; it is also soluble in dilute alkalis, yielding bluish-red solutions. Concentrated nitric acid at 15° converts *p*-nitrobenzeneazobenzoylacetone into a *nitrate*, which

crystallises in pale yellow needles; at 27° , nitration occurs, and a *p*-nitro-derivative, $\text{NO}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{N}_2 \cdot \text{CHAc} \cdot \text{CO} \cdot \text{C}_6\text{H}_4 \cdot \text{NO}_2$, is formed; this crystallises from boiling alcohol in yellow, felted needles melting at 198 — 199° , and dissolves readily in benzene, in concentrated sulphuric acid, or alkalis.

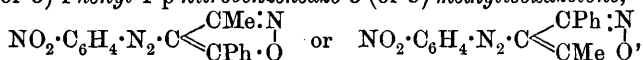
Two condensation products are formed when an acetic acid solution of equivalent quantities of *p*-nitrobenzeneazobenzoylacetone and phenylhydrazine is boiled for about half-an-hour. On the addition of a small quantity of water to the boiling solution, a product is obtained which, after several recrystallisations, melts at 211° to 212° , and is probably 1 : 3-diphenyl-4-*p*-nitrobenzeneazo-5-methylpyrazole,



the hot acetic acid filtrate from this product, on cooling, yields crystals of the second compound, which crystallises from alcohol in pale orange-red needles melting at 166 — 167° , and is probably 1 : 5-diphenyl-4-*p*-nitrobenzeneazo-3-methylpyrazole.

3-(or 5)-Phenyl-4-*p*-nitrobenzeneazo-5-(or 3)-methylpyrazolone, obtained when an aqueous alcoholic solution of *p*-nitrobenzeneazobenzoylacetone and semicarbazide sulphate is boiled for 2 hours, forms orange, glistening crystals melting at 241° , insoluble in dilute acids, but soluble in warm dilute alkalis; in small quantities, it may be distilled without decomposition.

5-(or 3)-Phenyl-4-*p*-nitrobenzeneazo-3-(or 5)-methylisoxazolone,



is obtained when nitrobenzeneazobenzoylacetone and hydroxylamine hydrochloride are heated in aqueous alcoholic solution for 4—5 hours; it crystallises in orange needles, melts at 192 — 193° , dissolves readily in alcohol, ether, or hot acetic acid, or in cold aromatic hydrocarbons. 3-(or 5)-*p*-Nitrophenyl-4-*p*-nitrobenzeneazo-5-(or 3)-methylisoxazolone, obtained from nitraniline-*p*-nitrobenzeneazonitrobenzoylacetone (melting at 198 — 199°) and hydroxylamine hydrochloride, crystallises in brownish needles melting at 172° .

2-*p*-Nitrophenyl-3-(or 5)-methyl-4-*p*-nitrobenzeneazo-5-(or 3)-phenylpyrazole, obtained when nitrobenzeneazobenzoylacetone is boiled for 60—80 hours with 15 per cent. hydrochloric acid, crystallises in brown, glistening plates melting at 221 — 222° , and dissolves in concentrated sulphuric acid, yielding an orange-red solution. J. J. S.

Hydrazones of Dithiocarbonates. By MAX BUSCH and E. LINGENBRINK (*Ber.*, 1899, 32, 2620—2622).—Dithiocarbazinic acid, $\text{R} \cdot \text{NH} \cdot \text{NH} \cdot \text{CS}_2\text{H}$, and its esters, $\text{R} \cdot \text{NH} \cdot \text{NH} \cdot \text{CS}_2\text{R}'$, react exclusively in the tautomeric form, $\text{R} \cdot \text{NH} \cdot \text{N} \cdot \text{C}(\text{SH})_2$ and $\text{R} \cdot \text{NH} \cdot \text{N} \cdot \text{C}(\text{SH}) \cdot \text{SR}$; acid hydrolysis decomposes the latter into phenylhydrazine and esters of dithiocarbonic acid.

The phenylhydrazone of dimethyldithiocarbonate is obtained as a yellow oil on digesting the sodium derivative of methyl phenyldithiocarbazine with methyl iodide in a closed vessel shielded from light; the hydrochloride is precipitated in a crystalline form by adding alcoholic hydrogen chloride to an ethereal solution of the oil. The

corresponding *dibenzyl* compound is prepared by heating benzyl phenyl-dithiocarbazinate with benzyl chloride and sodium hydroxide in alcoholic solution ; it separates as a viscid, yellow oil. G. T. M.

The Iodine Number of Proteids. By F. BLUM (*Zeit. physiol. Chem.*, 1899, 28, 288—299).—The amount of iodine capable of entering into intramolecular union in a proteid (by means of the Blum-Vaubel method) is designated its iodine number.

Experiments on a variety of proteids are given ; thus, 8.5 to 9 is the number for serum-globulin ; 10—11 for serum-albumin ; 7 for egg-albumin ; 12.5 for the nucleo-proteid of the pig's thyroid ; the proteid regarded by the author as the specific proteid of the thyroid (thyreo-toxalbumin), has an iodine number of only 6. W. D. H.

Reversible Liquefaction of Proteids. By TSVETT (*Compt. rend.*, 1899, 129, 551—552).—The swelling and dissolution in water of proteids is known to be facilitated by the action of acids, alkalis, and salts, and various organic substances, such as resorcinol, catechol, phenol, chloral hydrate, &c., are found to have the same effect. Gelatin dissolves to the extent of 3—4 per cent. in an 80 per cent. aqueous solution of resorcinol, whilst, if added in excess, two distinct liquid layers are obtained, the upper layer being a solution of gelatin in aqueous resorcinol, and the lower layer a solution of aqueous resorcinol in gelatin. The phenomenon is reversible, since the gelatin may be obtained in its original state by dialysis or by addition of water. Casein, hæmoglobin, peptones, plastin, and chloroplastin behave in a similar manner with resorcinol, whilst negative results were obtained with myosin, egg-albumin, and legumin. N. L.

Detection of Glutamic Acid amongst the Products obtained by decomposing Albumin of Animal Origin with strong Sulphuric Acid. By FR. KUTSCHER (*Zeit. physiol. Chem.*, 1899, 28, 123—131).—Although glutamic acid has been obtained in good yield by boiling animal proteids with hydrochloric acid and stannous chloride, it has not been isolated when sulphuric acid is the agent of hydrolysis ; this is because basic substances are formed at the same time in quantity more than sufficient to combine with the glutamic acid.

Casein was treated with sulphuric acid, a large part of the organic bases was precipitated with phosphotungstic acid, from the filtrate sulphuric and phosphotungstic acids were precipitated with just the required amount of baryta, and leucine and tyrosine were removed by crystallisation. The mother liquor, still slightly alkaline, was diluted, boiled, and saturated with copper carbonate ; it was then filtered, cooled, and precipitated with lead acetate ; the precipitate was collected and washed, suspended in water, and decomposed with hydrogen sulphide ; the filtered solution was concentrated to crystallisation. The crystals were dissolved in hot water and the solution saturated with copper carbonate, filtered, concentrated, and cooled ; the first few crystals that separated were free from copper, and were removed ; copper aspartate then crystallised. The mother liquor was decomposed with hydrogen sulphide, filtered, and concentrated, when

glutamic acid crystallised out. Some more of it is contained in the filtrate from the lead precipitate; in all, the casein yielded 1.8 per cent. of glutamic acid.

In the course of the investigation, a crystalline substance was obtained and analysed, which was apparently a compound of glutamic and aspartic acids, $5\text{C}_5\text{H}_9\text{O}_4\text{N}, \text{C}_4\text{H}_7\text{O}_4\text{N}$. C. F. B.

Products of the Peptic Digestion of Fibrin. By ERNST P. PICK (*Zeit. physiol. Chem.*, 1899, 28, 219—287).—This paper is the first of a series which appears to treat in a thorough way the properties, separation (by fractional precipitation with ammonium sulphate), analysis, &c., of the various products of the gastric digestion of fibrin. It is noticeable that in the ultimate analysis of proto- and hetero-albumose, with which the present paper is principally concerned, the numbers obtained, especially for carbon, differ considerably from those previously given by Kühne and Chittenden.

The following table compares the percentage composition of fibrin (Hammarsten) and the two proteoses just mentioned; the carbon and nitrogen are more, and the oxygen less, abundant than in the original fibrin.

	Fibrin.	Hetero-albumose.	Proto-albumose.
C.....	52.68	55.12	55.64
H	6.83	6.61	6.80
N	16.91	17.98	17.66
S.....	1.10	1.22	1.21
O.....	22.48	19.07	18.69

Both albumoses are carbohydrate-free, unlike fibrin, and both contain only easily separable sulphur. They differ from one another, not only in solubility, but also in the following ways: hetero-albumose contains 39, and proto-albumose 25, per cent. of its nitrogen in a basic form; proto-albumose yields tyrosine, indole, and scatole abundantly, hetero-albumose in traces only. Hetero-albumose yields abundance of leucine and glycocine; proto-albumose yields only a little leucine and no glycocine.

These two proteoses arise together from fibrin, but not one from the other. Both yield, on further gastric or pancreatic digestion, deutero-albumoses A and B, and peptone B. Deutero-albumose B, however, contains the carbohydrate radicle of the original fibrin, and must be looked on as a primary digestion product. The deutero-albumose B, which comes from proto- or from hetero-albumose, contains no carbohydrate radicle, and is a secondary product, or probably a mixture of two or more (B_1, B_2 , &c.). This confirms what has already been stated by Zunz (*Abstr.*, 1899, ii, 504). W. D. H.

Products of the Decomposition of Hæmatin. By WILLIAM KÜSTER (*Zeit. physiol. Chem.*, 1899, 28, 1—33).—In the preparation of hæmatin by Nencki's method, the yield can be increased by using amyl alcohol that has been employed already for the same purpose; the hæmin then obtained, however, is poorer in chlorine than is represented by the formula $\text{C}_{32}\text{H}_{31}\text{O}_3\text{N}_4\text{ClFe}$. In the conversion of

hæmin into hæmatin, the alkali must be allowed to act at the ordinary temperature; otherwise the product is poorer in carbon and hydrogen than the formula $C_{32}H_{32}O_3N_4Fe$ requires, although the amounts of nitrogen and iron remain the same.

Attempts to eliminate HCl from hæmin and obtain a compound $C_{32}H_{30}O_3N_4Fe$ by heating the former with aniline were unsuccessful.

The oxidation of hæmatin has been studied more carefully than hitherto (compare Abstr., 1899, i, 468), but no new products have been detected. With sodium dichromate (or calcium chromate) in acetic acid solution, the best result is obtained when 12 atoms of oxygen are used per mol. of hæmatin and the oxidation is effected at the ordinary temperature; about 40 per cent. is converted into the anhydride of tribasic hæmatic acid, $C_8H_8O_5$, and dibasic hæmatic acid, $C_8H_9O_4N$ (Abstr., 1896, i, 516), of which the former is present in larger amount; 40 per cent. is obtained in the form of a substance insoluble in water and still containing iron, which yields small quantities of $C_8H_8O_5$ when further oxidised with alkaline permanganate; a small quantity of carbon dioxide is also formed, and some ammonia, more of which is produced in proportion as the yield of $C_8H_8O_5$ is greater and that of $C_8H_9O_4N$ less. When the oxidising agent employed is potassium ferricyanide in strongly alkaline solution, at first at the ordinary temperature, then on the water-bath, 8—12 atoms of oxygen being used, the iron separates as hydroxide, a little $C_8H_8O_5$ is formed, and also a substance, insoluble in water, which much resembles hæmatin and again yields small quantities of $C_8H_8O_5$ when subjected to further treatment. With ammonium persulphate (equal to 20 atoms oxygen) as the oxidising agent on the water-bath, ammonia and a little hydrogen cyanide are evolved, iron hydroxide is precipitated, and apparently succinic acid and traces of volatile acids are formed.

It is suggested that hæmatin may be regarded as constituted according to the scheme $FeR_2R^1_2$, where R and R^1 are complexes containing each 8 atoms of carbon. Hæmatoporphyrin is then RR^1 , and the products of the oxidation of hæmatin are $FeR^1_2 + R + R$.

C. F. B.

Preparation and Products of Decomposition of Hæmatoporphyrin. By WILLIAM KÜSTER and MARTIN KÖLLE (*Zeit. physiol. Chem.*, 1899, 28, 34—39. Compare Abstr., 1897, i, 232).—Hæmatoporphyrin is oxidised much less readily than hæmatin (preceding abstract) by sodium dichromate in acetic acid solution; the products are dibasic hæmatic acid, $C_8H_9O_4N$, and substances, insoluble in water, of which the composition corresponds approximately with $C_{14}H_{14}O_8N_2$ and $C_{14}H_{16}O_5N_2$. Dibasic hæmatic acid is shown by titration with ammonia to be really monobasic; when the ammonium salt is boiled with aqueous caustic soda, not one, but two mols. of ammonia are eliminated, and a salt of tribasic hæmatic acid, $C_8H_{10}O_6$, is formed; the anhydride of this acid is the substance $C_8H_8O_5$.

In the preparation of hæmatoporphyrin from hæmin by Schalféeff's method, a bye-product, insoluble in water, is obtained; this has approximately the composition $C_{32}H_{36}O_5N_4$.

C. F. B.

Blue Pigment in Coral (*Heliopora Cœrulea*) and other Animal Organisms. By ARCHIBALD LIVERSIDGE (*Chem. News*, 1899, 80, 29—31; 41—43).—The pigment in blue coral was isolated by treatment with hydrochloric acid to remove the calcium carbonate, and extraction of the residue with 75 per cent. alcohol or acetic, formic, or propionic acid. On evaporation of the solvent, a dull, dark green mass was obtained. The behaviour of the pigment with a very large number of solvents and reagents was investigated, but no crystalline product was obtained. Comparison with other blue animal pigments seemed to show that this substance was not identical with any of them.

D. A. L.

Pyocyanin, the Blue Colouring Matter of *Bacillus Pyocyaneus*. By G. W. BOLAND (*Chem. Centr.*, 1899, ii, 265; from *Centr. Bakt. Parasitenk.*, [i], 25, 897—902).—Pyocyanin is best obtained from cultures of *Bacillus pyocyaneus* in peptone-agar agar or peptone-gelatin, as in these cases it is free from the fluorescent colouring matter which is always formed in cultures containing glycerol; it is extracted with chloroform. The solution in chloroform gradually becomes green and finally yellow, Fordos' pyoxanthin or pyoxanthose being formed; this change is also quickly effected by exposing the solution to sunlight. Since the aqueous solution under similar conditions remains unchanged, the formation of pyoxanthose is probably due to the liberation of chlorine, and this view was experimentally confirmed. The green colouring matter formed intermediately is a mixture of pyocyanin and pyoxanthose, and from a solution of these compounds in chloroform, hydrochloric acid (1 : 3) dissolves only the former whilst most of the latter may be extracted by sulphuric acid (1 : 3). Pyoxanthose crystallises in thick, microscopic needles. The reddish-brown colouring matter which is found in the culture together with pyocyanin is insoluble in chloroform, ether, alcohol, benzene, xylene, or carbon disulphide, but may be extracted by means of alkalis or barium hydroxide. Potassium hydroxide, which also extracts the fluorescent colouring matter, is the best solvent. The quantity of pyocyanin formed in the culture increases to a maximum in several days, remains constant for ten days and then gradually decreases, the reddish-brown colouring matter increasing proportionately until it alone is present.

Bacillus pyocyaneus probably forms only two colouring matters, pyocyanin and the fluorescent dye, the latter being also produced by many other bacteria. The pyocyanin is gradually oxidised to pyoxanthose by the oxygen of the air, whilst in the culture itself it is converted into a reddish-brown colouring matter.

E. W. W.

Ovarian Colloid. By THEODOR PANZER (*Zeit. physiol. Chem.*, 1899, 28, 363—381).—The jelly-like substance which occurs in certain forms of ovarian cystoma has been named pseudomucin, paramucin, &c. It gives the ordinary proteid tests; it contains 93.1 per cent. of water, 5.7 per cent. of organic, and 1.2 per cent. of inorganic substances; among the inorganic constituents, sodium and chlorine are the most abundant. The principal organic constituent, the colloid, has the following percentage composition: C, 47.27; H, 5.86; N

8.40; S, 0.79; P, 0.54; ash, 6.43; iodine is absent. This agrees very well with Mitjukoff's analyses. The phosphorus is probably in the ash. By treatment with dilute sulphuric acid, a reducing but non-fermentable substance is obtained, which is probably allied to the reducing substance obtainable from cartilage. On decomposition, the proteid matter yields ammonia, leucine, humous substances, and traces of hexon bases.

W. D. H.

Pseudo-nucleins. By K. H. GIERTZ (*Zeit. physiol. Chem.*, 1899, 28, 115—122).—Artificial pseudo-nuclein is a salt-like combination of albumin with metaphosphoric acid; by dissolving it in water containing alkali, it is decomposed into alkali phosphate and albumin; the latter is probably present as a soluble alkali-albumin. The pseudo-nuclein from casein or vitellin contains no metaphosphoric acid which can be split off in this way, and is therefore not identical with the artificial nuclein.

W. D. H.

Histon-like Substance from the Thymus. By A. FLEROFF (*Zeit. physiol. Chem.*, 1899, 28, 307—312).—A histon-like proteid was obtained by extracting a thymus gland which had been under alcohol and ether with 2 per cent. sulphuric acid. Its percentage composition is C, 51.77; H, 8.06; N, 17.72; S, 1.99; O, 20.46. It gives the typical reactions of a histon. The acid also extracts a substance from the gland (parahiston) which is soluble after precipitation in excess of ammonia. A third substance was separated from parahiston during its purification with alcohol; it is sparingly soluble in alcohol, and precipitates a solution of Witte's peptone, but its nature was not determined.

W. D. H.

Decomposition Products of Histon from Leucocytes. By D. LAWROFF (*Zeit. physiol. Chem.*, 1899, 28, 388—398).—Histon prepared from thymus (see preceding abstract), when decomposed by hydrochloric acid, yields the three hexon bases, histidine, arginine, and lysine, which together account for 25 per cent. of its weight. Arginine is the most abundant. Both the hydrochloride and carbonate of lysine are dextrorotatory; so also are arginine and its hydrochloride. Details are given in full.

W. D. H.

Histidine. By ALBRECHT KOSSEL and FR. KUTSCHER (*Zeit. physiol. Chem.*, 1899, 28, 382—387).—Hedin (*ibid.*, 22, 193) states that histidine is optically inactive; this is not so, the free base being lævorotatory $[\alpha]_D - 39.74$, whilst its salts are dextrorotatory, ($C_6H_9O_2N_3.HCl$, +1.74; $C_6H_9O_2N_3.2HCl$, +5.3 to 6.4). There is, moreover, no difference between Hedin's and the authors' histidine in crystallographic and boiling point investigations. Full details of the examination of the crystals of histidine dichloride are given.

W. D. H.

Decomposition Products of Conchiolin. By G. WETZEL (*Chem. Centr.*, 1899, ii, 59; from *Centr. Physiol.*, 13, 113—114).—According to Krukenberg (*Abstr.*, 1885, 826), when conchiolin is heated with acids, leucine, leucinimide, and a substance which crystallises in transparent prisms are formed, but tyrosine is not obtained. The

author finds, however, that, by the action of acids on conchiolin prepared from the shells of *Mytilus galloprovincialis*, leucine, glycocine, and tyrosine are obtained, but not leucinimide. E. W. W.

Lilienfeld's Synthesis of Peptone. By MARTIA KLIMMER (*Pflüger's Archiv*, 1899, 77, 210—214).—Lilienfeld's so-called synthesised peptone was prepared and compared with true peptone. The artificial condensation product is not peptone; it does not give the biuret reaction, and is easily decomposed into its two constituents, phenol and aminoacetic acid. W. D. H.

Antipeptone. By FR. KUTSCHER (*Zeit. physiol. Chem.*, 1899, 28, 88—97. Compare Abstr., 1898, i, 611; 1899, i, 179).—The paper, is largely controversial, and deals especially with the work and views of Kühne and of Siegfried. The author brings forward fresh experiments to support his contention that the so-called antipeptone is a mixture of several simple substances. W. D. H.

Protamines. By N. MORKOWIN (*Zeit. physiol. Chem.*, 1899, 28, 313—317).—The hitherto known protamines obtained from the sperm of various fishes have been named salmine, clupeine, scombrine, sturine, and arbacine. On decomposition, they yield the hexon bases, arginine, histidine, and lysine. A new protamine prepared from the sperm of the sea-hare (*Cyclopterus lumpus*) is now described; it is termed cyclopterine. It differs from the others by giving Millon's reaction, and also in percentage composition. It is not contaminated with peptone, although probably it is a loose compound of true protamine with a peptone-like material. It thus forms a link between the protamines and the proteids proper. W. D. H.

Epinephrine. By JOHN J. ABEL (*Zeit. physiol. Chem.*, 1899, 28, 318—362. Compare Abstr., 1899, i, 395).—Epinephrine, the substance in the suprarenals which raises blood pressure, is alkaloidal. It may be isolated from aqueous extracts of the gland as a benzoyl compound, $C_{17}H_{14}O_4NBz$; on isolating the base from this, it loses most of its physiological activity. It yields a *hydrochloride*, *hydrobromide*, *picrate*, and a *triacetyl* derivative, $C_{17}H_{12}O_4NAc_3$, appears to be related to substances of the pyrrole or scatole group, and may have the constitution $C_6H_4 \begin{smallmatrix} NH \\ \diagup \diagdown \\ CMe \end{smallmatrix} > C \cdot CH(OH) \cdot CO \cdot C_6H_3(OH_2)$. When fused with alkali, it yields scatole. On treatment with dilute alkalis, it yields a dark pigment, epinephric acid, and a product of basic nature, not defined at present, but having a coniine or pyridine-like smell. Normally, epinephrine possibly leaves the body in the urine as uroerythrin. W. D. H.

Organic Chemistry.

The Wax of Bacillariaceæ and its Connection with Petroleum. By GUSTAV KRÄMER and ADOLF SPILKER (*Ber.*, 1899, 32, 2940—2959).—Bacillariaceæ (diatoms) are known to contain drops of oil distributed in the plasma, and from peat, in which diatoms occur largely, 1·5—4 per cent. of a wax can be extracted which contains 10—11 per cent. of sulphur. In the Uckermark, to the west of Stettin, the bed, some 23 feet in thickness, of a lake, which was drained long ago, consists chiefly of diatoms, and from it a wax can be extracted. This melts at 50—70°, resembles ozokerite in appearance, contains C, 73·5; H, 11·2; S, 1·0, and ash, 2·4 per cent., from which it may be concluded that the wax contains oxygen and consists of esters of organic acids. Fuming nitric acid does not attack the wax in the cold, but dissolves 38 per cent. on heating; from the residue, lekene, which occurs in ozokerite (Beilstein and Wiegand, *Abstr.*, 1883, 1073), can be isolated.

These waxes much resemble ozokerite. The latter contains only 0·15 per cent. of sulphur, however; only traces of it are hydrolysed by alcoholic potash, and when it is distilled no water is formed and the gas evolved contains no oxides of carbon and but little hydrogen sulphide. Of the wax from the lake silt, on the other hand, about 10 per cent. undergoes hydrolysis; and on distillation of the peat-wax, water is formed and the gas evolved contains 10 per cent. of hydrogen sulphide together with carbon dioxide and monoxide. When ozokerite is distilled under a pressure of 20—25 atmos., the gas evolved consists of methane and olefines, along with traces of hydrogen sulphide and carbon dioxide; the gas obtained from the silt-wax in similar circumstances contains hydrogen sulphide and carbon dioxide and monoxide, and that from carnauba- and Japan-wax contains both oxides of carbon. In all cases, a large part of the distillate boils at 130—290°, and this fraction has the character of the paraffins; its composition is C, 84·4—85·0, and H, 15·1 per cent., and its molecular weight is 149—169 determined cryoscopically in benzene solution ($C_{11}H_{24}$ requires C, 84·7; H, 15·3; molecular weight, 156). A similar fraction from petroleum (from the Tegernsee) had a like composition. It is further found that the composition of the strata overlying the ozokerite deposits of Eastern Galicia and the petroleum beds of the Tegernsee contain the same mineral constituents as the lake silt.

The following theory of the origin of petroleum is then developed. Lakes became filled up in the process of time with a growth of diatoms; over this growth other deposits were formed subsequently. The decay of the diatoms (which takes place very slowly) gave rise to ammonium carbonate, which hydrolysed the wax present; from the resulting acids, carbon dioxide and monoxide and water were eliminated, and ozokerite formed. Where the pressure was small and the temperature low, this was converted further into a comparatively low boiling petroleum; under greater pressure and higher temperature, the sulphur present

also exerting an influence, a petroleum was formed which contained a large proportion of viscid, high-boiling substances (probably formed by polymerisation of olefines); more extended action of the sulphur, and of atmospheric oxygen, gave rise to a petroleum containing much asphalt. Generally speaking, the petroleum would be absorbed by the sandy bed of the lake; occasionally it might be absorbed by a calcareous bed, a deposit of asphalt being thus formed. C. F. B.

Heptane contained in Grosny Naphtha. By K. W. CHARIT-SCHKOFF (*Chem. Centr.*, 1899, ii, 474; from *J. Russ. Chem. Soc.*, 1899, 31, 552—554).—The benzene boiling at 84—100°, obtained from the naphtha of Grosny, contains an *isoeptane*, C_7H_{16} , which boils at 90·5—91·5°, and has a sp. gr. 0·7158 at 15°. This naphtha only contains a very small amount of normal heptane. The interpretation of the curves representing relationships of boiling point and specific gravity is discussed in the original paper, the author inclining to Aschan's, rather than to Markownikoff's, views. E. W. W.

Action of Acetylene on Oxides of Copper. By FRANK A. GOOCH and DE FOREST BALDWIN (*Amer. J. Sci.*, 1899, [iv], 8, 354—358). Compare Erdmann and Köthner, *Abstr.*, 1899, i, 21).—Several errors in calculation are pointed out in Erdmann and Köthner's communication. The experiments have been repeated, and the conclusion arrived at is that Erdmann and Köthner's "Kupferacetylen" is nothing less than a hydrocarbon or hydrocarbons mixed with copper or an oxide of copper. The amount of copper found varies considerably (1·54 to 24·21 per cent.) with the conditions of the experiment. When cuprous oxide is employed, a temperature of 225° is the most favourable; similar results may be obtained with cupric oxide, but copper itself is not acted on until much higher temperatures are reached.

Oxide of silver is acted on at the ordinary temperature, and, as a rule, an explosion occurs. J. J. S.

NOTE.—The same conclusion as to the nature of Erdmann and Köthner's compound has been arrived at by Alexander (*Abstr.*, 1899, i, 843). J. J. S.

Preparation of Tetrachloromethane. By E. SERRA (*Gazzetta*, 1899, 29, ii, 353—354).—Details are given of the method employed for the preparation of tetrachloromethane free from carbon disulphide and from chloroform, which are very difficult to entirely remove.

T. H. P.

Isomeric Compounds, $C_6H_8O_4N_4$, from Acetylmethylnitrolic Acid. By CARL STEFFENS (*Annalen*, 1899, 309, 241—253).—Acetylmethylnitrolic acid, $COMe \cdot C(NO_2) \cdot NO_2$, obtained by oxidising acetone with nitric acid, yields two compounds having the empirical formula $C_6H_8O_4N_4$; one melts at 191°, and is produced by converting acetylmethylnitrolic acid into nitromethylglyoxime, and heating the latter with sodium hydrogen carbonate (Behrend and Schmitz, *Abstr.*, 1894, i, 109), whilst the other, melting at 140°, is derived by the agency of hydroxylamine from the product of heating acetylmethylnitrolic acid

(Behrend and Tryller, Abstr., 1895, i, 201). The author has attempted to establish the constitution of these two substances.

The derivative melting at 191° , referred to as Schmitz's compound, probably has the constitution represented by the formula $\text{NOH}:\text{CMe}\cdot\text{C}\begin{smallmatrix} \text{N}\cdot\text{O} \\ \diagup \quad \diagdown \\ \text{O}\cdot\text{N} \end{smallmatrix}\text{C}\cdot\text{CMe}:\text{NOH}$. The hydrochloride is decomposed by hot water, yielding the original substance, which dissolves in hot hydrochloric acid, liberating carbon dioxide; the remaining products are α -isonitrosopropionic acid, ammonia, hydroxylamine, and acetic acid. The *diacetyl* derivative crystallises from alcohol in needles and melts at 141° ; the *dibenzoyl* derivative becomes brown at 200° and melts at 220 — 225° , when it decomposes. The compound dissolves in alkali (2 mols.), and is reprecipitated by acids from a freshly prepared solution, but after an interval, acids do not yield a precipitate; it immediately reduces potassium permanganate.

The isomeride called Tryller's compound may have the constitution $\text{NOH}:\text{CMe}\cdot\text{C}\begin{smallmatrix} \text{N} \\ | \\ \text{N}\cdot\text{O}\cdot\text{O}\cdot\text{N} \end{smallmatrix}\text{C}\cdot\text{CMe}:\text{NOH}$. The hydrochloride readily yields

the original substance, which gives rise to carbon dioxide, oxalic acid, ammonia, hydroxylamine, and acetic acid when treated with boiling acids; there is produced also a small quantity of a volatile ketone, probably the ketone of which Tryller's compound is the dioxime. The *dibenzoyl* derivative crystallises in slender, white needles and melts at $155\cdot5$ — $156\cdot5^{\circ}$. The *anhydride*, $\text{C}_6\text{H}_6\text{O}_3\text{N}_4$, obtained by acidifying a solution in caustic soda which has been boiled for some time, crystallises from alcohol in lustrous, yellowish leaflets and melts at 188 — 190° , becoming brown at 150° .
M. O. F.

Phosphoric Esters. By JACQUES CAVALIER (*Ann. Chim. Phys.*, 1899, [vii], 18, 449—507. Compare Abstr., 1894, i, 484; 1895, i, 638; 1896, ii, 590; 1897, i, 310; 1898, i, 616, ii, 499; 1899, i, 558, ii, 13, 55).—A detailed account of work already published.

G. T. M.

Manufacture of Glycerophosphate. By MARCEL GUÉDRAS (*Chem. Centr.*, 1899, ii, 626; from *Mon. Sci.*, [iv], 13, II, 577—580).—Commercial glycerophosphate, $\text{CaPO}_3\cdot\text{O}\cdot\text{C}_3\text{H}_5(\text{OH})_2$, prepared by heating phosphoric acid with glycerol for a day at 150° and then for 3 days at 115 — 125° , and treating the glycerophosphoric acid with milk of lime, is alkaline towards litmus, but neutral to phenolphthalein, dissolves in about 25 parts of water, leaving a small quantity of insoluble calcium phosphate, and is precipitated from its aqueous solution by heating. Boiling alcohol usually extracts some glycerol and phosphoric acid. Sodium and potassium glycerophosphates are syrupy liquids. The magnesium salt is a powder, and has properties similar to those of the calcium salt. The iron salt, prepared by digesting crude glycerophosphoric acid with iron dust below 60° , crystallises in leaflets which have a golden lustre. Quinine glycerophosphate, $\text{C}_3\text{H}_7\text{O}_2\cdot\text{O}\cdot\text{PO}(\text{OH})_2\cdot(\text{C}_{20}\text{H}_{24}\text{O}_2\text{N}_2)_2 + 4\text{H}_2\text{O}$, is slightly soluble in water, more so in alcohol, and may be used as a substitute for quinine sulphate.
E. W. W.

Esters of Tungstic Acid. By EDGAR F. SMITH and CLAUDE DUGAN (*J. Amer. Chem. Soc.*, 1899, **21**, 1016—1017. Compare Goessmann, *Annalen*, 1857, **101**, 218; Maly, *ibid.*, 1866, **139**, 240).—When Maly's method is employed for the preparation of esters of tungstic acid, the products obtained consist of a mixture of hydrated tungstic acid and an incompletely esterified product: for example, with tungsten oxychloride and isobutyl alcohol, a product, $3\text{WO}_3 \cdot 2\text{H}_2\text{O} + \text{WOCl}_2(\text{OC}_4\text{H}_9)_2$, was obtained, which was soluble in dry ether, but was reprecipitated on the addition of pure ethyl alcohol. J. J. S.

Action of Water on certain Fatty Acids. By EDWIN DE BARR (*Amer. Chem. J.*, 1899, **22**, 333—349).—The author has studied the rate of interaction of water with certain halogenated fatty acids at 150° , 3 mols. of water being used for each halogen atom present. Tables of values are given and curves plotted, which show the rate of displacement of the halogen atoms from γ -chlorobutyric, β -chloropropionic, trichloroacetic, β -chlorobutyric, chloroacetic, dichloroacetic, α -chloropropionic, α -bromopropionic, α -bromobutyric, and α -chlorobutyric acids; the relative ease with which the halogen is removed from the various acids is given by the order in which these are named. This order is, except in the cases of mono-, di-, and trichloroacetic acids, not the same as that of the affinity constants. Most of the acids begin to undergo secondary change before the displacement of the halogen is complete; the relative stability of the compounds at 150° under pressure and in presence of hydrogen chloride appears to be in the order, α -bromopropionic (7.06), α -chlorobutyric (7.50), α -bromobutyric (9.25), α -chloropropionic (11.41), dichloroacetic (17.76), β -chlorobutyric (37.38), chloroacetic (47.11), β -chloropropionic (50.49), trichloroacetic (100.00), and γ -chlorobutyric acids (100.00), the numbers attached to each acid showing the percentage of halogen displaced before decomposition begins. On comparing this list with the foregoing, it appears that those acids which are most stable react the most rapidly with water, whilst those which are least stable react most slowly.

It appears, moreover, that with the α -acids containing the same halogen, the rate of displacement of the latter diminishes in passing from acetic acid to its higher homologues; the same holds true with the β -acids, and a similar law regulates the total amount of transformation occurring before decomposition begins. It is especially noteworthy that the further a halogen atom is removed from the carboxyl group in the same acid, the more easily is it displaced under the influence of water; thus, the amount of halogen replaced after half an hour is 4.42 per cent. of the total in the case of α -chloro-, and 41.5 per cent. in the case of β -chloropropionic acid.

β -Chloropropionic acid is best prepared by the action of chlorine on β -iodopropionic acid, and melts at 61° , not at 35.5° to 58° as has formerly been stated; it boils at 204° . β -Chlorobutyric acid, prepared by saturating an ethereal solution of crotonic acid with hydrogen chloride at 0° , and subsequently leaving it in a sealed tube for 24 hours at the ordinary temperature, melts at 16 — 16.5° , boils at 116° under 22 mm. pressure, and is entirely free from α -acid. γ -Chloro-

butyric acid, prepared similarly from trimethylenecarboxylic acid, melts at 12° and boils at 196° under 22 mm. pressure. W. A. D.

Electrolytic Oxidation of Succinic Acid. By CHARLES H. CLARKE and EDGAR F. SMITH (*J. Amer. Chem. Soc.*, 1899, 21, 967—972).—The electrolytic oxidation of succinic acid in solutions containing known quantities of sodium hydroxide and of alcohol, has been studied. A divided cell was employed and a current density of from 0.024 to 1.55 ampères per 100 sq. cm. of anode surface. The products found were tartaric, oxalic, and carbonic acids, oxygen, carbon monoxide, ethylene, and methane, together with some aromatic substances. A colouring matter, soluble in ether and melting at 178° , has also been isolated. J. J. S.

Separation and Purification of Sugars. By OTTO RUFF and GERHARD OLLENDORFF (*Ber.*, 1899, 32, 3234—3237).—Phenylbenzylhydrazine is better adapted for the isolation of sugars than phenylhydrazine itself, because of the ready formation and insoluble character of the hydrazones produced, and this substance has already been employed by Lobry de Bruyn and Alberda van Ekenstein (*Abstr.*, 1896, i, 588; 1897, i, 41). *l*-Xylosephenylbenzylhydrazone melts at 99° (corr.), and dissolves in about 1000 parts of water. *d*-Arabinosephenylbenzylhydrazone melts at 174° (corr.), and is almost insoluble in water. The corresponding hydrazone of dextrose melts at 165° (corr.), and not at 150° as stated by these authors. The sugars are best regenerated from these hydrazones by treatment with formaldehyde, removal of the formaldehydephenylbenzylhydrazone by ether, and repeated evaporation of the solution to remove the excess of formaldehyde.

Formaldehydephenylbenzylhydrazone crystallises in white needles melting at 41° . A. H.

Isomaltose. By HENRI POTTEVIN (*Ann. de l'Inst. Pasteur*, 1899, 13, 796—800).—From a solution of pure maltose and a non-reducing dextrin, the author has prepared an osazone which melts at 154° and crystallises in tufts of very slender needles. From this fact, and a consideration of previous work, he concludes that Lintner's isomaltose is a mixture of maltose and a dextrin (compare Ling and Baker, *Trans.*, 1895, 67, 704, 739; 1897, 71, 511; Brown and Morris, *Trans.*, 1895, 67, 709). H. R. LE S.

Crystallised Melibiose. By ARMINIUS BAU (*Chem. Centr.*, 1899, ii, 526; from *Woch. Brauerei*, 16, 397—400).—Melibiose was prepared by fermenting a solution of melitriose by means of a pure culture of a top-fermenting yeast. After decolorising the solution of the product with animal charcoal, it was evaporated and the melibiose precipitated from the residual syrup after filtering, by means of ether and purified by conversion into the barium compound, &c. Melibiose forms triclinic crystals containing $2\text{H}_2\text{O}$, is not hygroscopic, and is not changed by exposure to the air; it is easily soluble in water or methyl alcohol, and, like its aqueous solution, decomposes at 80° . It sinters at 82 — 83° , partially melts at 84 — 85° , and has a specific rotatory power $[\alpha]_D +129.38^{\circ}$ at 20° ; freshly prepared solutions give a

slightly lower value for the last constant. Its power of reducing Fehling's solution, calculated on the dry substance, is only 92—95 per cent. as much as that of maltose, and it is neither hydrolysed nor fermented by top-yeasts, but is decomposed by bottom-yeasts, forming dextrose and *d*-galactose, which are completely fermented.

E. W. W.

Rhamninoase. By CHARLES TANRET and GEORGES TANRET (*Compt. rend.*, 1899, 129, 725—728).—It has been previously shown that xanthorhamnin, the glucoside of *Rhamnus infectoria*, is converted by the action of dilute acids into a mixture of rhamnetin, rhamnose, and galactose, the last-named compounds being themselves the products of hydrolysis of an intermediate saccharose, for which the name *rhamninoase* is now proposed. Rhamninoase, which is best obtained by the action of the ferment rhamnase, or, as it is more properly termed, rhamninase, on xanthorhamnin at 70°, is slowly hydrolysed by dilute acids into two mols. of rhamnose and one of galactose. It has a slightly sweet taste, and is soluble in all proportions in water, and very soluble in strong alcohol. It has a rotatory power $[\alpha]_D - 41^\circ$, and melts and slowly decomposes at 140°; it has not been obtained crystalline. Rhamninoase has one-third the reducing power of dextrose. Ordinary yeast, invertase, emulsin, and the ferments of *Aspergillus* have no action on it. No insoluble osazone or phenylhydrazone could be obtained from it. When treated with sodium amalgam in the cold, rhamninoase takes up two atoms of hydrogen and is converted into a new sugar, *rhamninite*, $C_{18}H_{34}O_{14}$, which has a rotatory power $[\alpha]_D - 57^\circ$, and yields rhamnose and dulcitol on hydrolysis. Rhamninoase is oxidised by nitric acid to mucic and galactonic acids, and by bromine to *rhamninostrionic acid*, $C_{18}H_{32}O_{15}$. This acid is monobasic and bears the same relation to rhamninoase that lactobionic acid does to lactose. It has a rotatory power $[\alpha]_D - 94^\circ$, but does not reduce Fehling's solution; both it and its salts are amorphous. On hydrolysis, it yields two mols. of rhamnose and one of galactonic acid.

N. L.

Constitution of Starch. By WIKTOR SYNIEWSKI (*Annalen*, 1899, 309, 282—315. Compare Abstr., 1898, i, 551).—From experiments with potato starch, the author draws the following conclusions:

1. Potato starch granules consist of an individual substance having the empirical formula $C_6H_{10}O_5$.

2. Hydrolysis of potato starch can proceed in two ways, namely, carbinol-hydrolysis, in which addition of water to the anhydride of two carbinol groups takes place, and carbonyl-hydrolysis, in which at least one of the two groups forming the anhydride is a carbonyl radicle.

3. The compound obtained from potato starch by the action of boiling water under atmospheric or increased pressures, caustic potash, or sodium peroxide, is the result of carbinol-hydrolysis; it does not reduce Fehling's solution.

4. The simplest product of carbinol-hydrolysis is amylogen, $C_{54}H_{96}O_{48}$. The molecules of starch, and of all products of carbinol-hydrolysis standing between starch and amylogen, consist of a number of amyl-

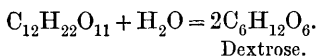
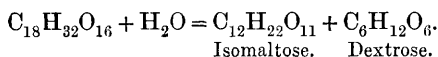
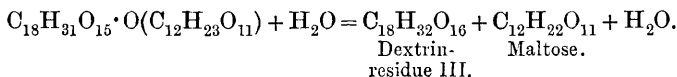
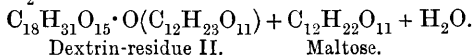
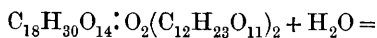
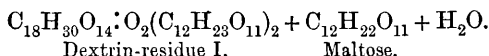
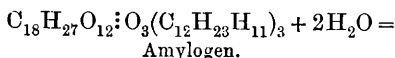
ogen molecules associated in the form of anhydrides by elimination of water from carbinol groups.

5. The composition of all such compounds may be expressed by the general formula $(C_{54}H_{96}O_{48})_n - (3n - x)H_2O$, in which n is unknown, and x is variable from 0 to $3n$.

6. Amylogen consists of three maltose residues, combined with a dextrin containing 18 atoms of carbon. The dextrin is composed of three glucose residues, of which two are in the form of an isomaltose residue.

7. The first stage in the hydrolysis of amylogen is the separation of the maltose molecules from one another and from the dextrin; further action of malt extract on the latter resolves it into glucose and isomaltose, which finally yields a further quantity of glucose.

8. Diastatic hydrolysis of amylogen gives rise to intermediate products, the changes being represented by the following equations:



9. Diastatic decomposition of those products of carbinol-hydrolysis of starch which contain many amylogen molecules yields a large number of dextrinous compounds, of which those containing the dextrin-residues I, II, and III are typical.

The author uses the name dextrin for all products of starch hydrolysis excepting sugars, and indicates as amylo-dextrins those which proceed from starch by carbinol-hydrolysis, and are therefore indifferent towards Fehling's solution, and develop the familiar starch blue with a solution of iodine in potassium iodide; the residual dextrin produced from amylo-dextrin by eliminating all the maltose is called "*Grenz-dextrin*." Dextrins between the latter and amylo-dextrins are called maltodextrins, and those derived from "*Grenz-dextrin*" by withdrawing dextrose residues are called glucodextrins.

M. O. F.

Preparation of Starch Solutions and Separation of Starch Granules from such Solutions. By HERMANN RODEWALD and A. KATTEIN (*Chem. Centr.*, 1899, ii, 419; from *Sitzungsber. Akad. Wiss. Berlin*, 24, 628—630).—When a solution of iodine in potassium iodide

is poured over potato, wheat, or rice starch and the mixture (which should contain 15 parts of iodine and 200—300 of water for every 100 of starch) heated for 15 minutes at 130° , a greenish-brown liquid is formed which consists mainly of excess of iodine solution with very small quantities of starch iodide and some sugar. The starch iodide grains, when examined under the microscope, appear to have been changed, and are soluble in water. The starch iodide may be separated by dialysing, and the blue solution so obtained forms a clear filtrate. This solution contains about 2 per cent. of the iodide and an amount of iodine corresponding with 14.3—14.85 per cent. of iodine in the iodide. When the solution is evaporated over a naked flame, the starch iodide separates and iodine is liberated; the latter may be removed by treatment with steam, and a clear or very slightly turbid solution of starch is then obtained. When the solution is slowly cooled, a white precipitate is formed, and this, when examined under the microscope, appears to consist of almost spherical starch granules. A similar precipitate is formed by all varieties of starch. The filtrate contains starch and gives an intense blue coloration with iodine; the blue compound may be separated by adding potassium iodide.

The starch granules which separate from the solution also give a blue coloration with iodine, and after drying are insoluble in cold water, and are only gelatinised with difficulty by boiling water. Potassium hydroxide also reduces the granules to paste. E. W. W.

Saccharification of Starch. By HENRI POTTEVIN (*Ann. de l'Inst. Pasteur*, 13, 1899, 665—688).—The dextrans obtained from starch by the action of amylase may be divided into three groups. (1) Achroodextrans, (2) amylo dextrans, and (3) erythro dextrans. With the first, starch produces no coloration, but with the second, a blue, and with the third a red coloration is obtained. No red coloration is produced when starch is added to a mixture of achroodextrin and amyloextrin, so that Solomon's statement that erythro dextrans do not exist, but are mixtures of achroodextrans and amylo dextrans is erroneous. Musculus' statement that amylo dextrans in concentrated solutions give a blue coloration with starch and a red coloration in dilute solutions is also erroneous, because, whatever the dilution, a blue colour is always produced. Amyloextrin itself is not a single substance, for by careful precipitation with alcohol two dextrans have been obtained from it. The first, α -amyloextrin, gives opalescent solutions, which on warming become somewhat viscous, but on cooling again become opalescent. Its blue compound with iodine is readily precipitated by a 1 per cent. solution of sodium chloride. The second, or β -amyloextrin, gives solutions which are viscous in the cold, and its compound with iodine is not precipitated by even a 20 per cent. solution of sodium chloride. The formation of dextrin from starch by the action of amylase is quite independent and distinct from the formation of maltose from the dextrin, for a solution may be prepared in which the formation of dextrin is still going on whilst that of maltose has completely stopped.

When amylase acts on starch, the rate of saccharification rapidly

decreases. This is due to the fact that the starch granules are not all of the same size, the larger ones being readily attacked by amylase, whereas the smaller are only attacked with difficulty.

H. R. LE S.

Maltodextrin. By HENRI POTTEVIN (*Ann. de l'Inst. Pasteur*, 1899, 13, 728—734).—The method of fermentation adopted by Brown and Morris to show that maltodextrin is not fermentable with yeast, is here objected to, since no precautions were taken to render the fermenting liquid aseptic, or to prevent the subsequent introduction of microbes during the fermentation. Using carefully sterilised and aseptic solutions, the author confirms the statement of Brown and Morris that maltodextrin is not fermentable, but points out that this is no evidence that maltodextrin is not a mixture, because a mixture can be made of pure maltose and a suitable dextrin, which, like maltodextrin, is not fermentable with yeast. Dextrins soluble in 70 per cent. alcohol retard the fermentation of maltose much more than those which are soluble in more dilute alcohol solutions. By careful fractional precipitation of a solution of maltodextrin by means of alcoholic solutions of varying strengths, precipitates of different composition are obtained, those obtained by precipitation with 58 per cent. alcohol consisting of 20 per cent. of maltose and 80 per cent. of dextrin, whereas with 94 per cent. alcohol the precipitate contains 70 per cent. of maltose and 30 per cent. of dextrin. A mixture of pure maltose and a dextrin (soluble in 70 per cent. alcohol) dialyses in exactly the same way as a solution of maltodextrin. The mere fact that maltodextrin dialyses as a whole is therefore no proof that it is a single substance.

Those dextrins soluble in dilute alcohol dialyse more quickly than those which are only soluble in strong alcohol.

H. R. LE S.

Preparation and Estimation of Glycogen. By ARMAND GAUTIER (*Compt. rend.*, 1899, 129, 701—705).—The process described, which serves for both the preparation and estimation of glycogen, is based on the fact that the nitrogenous substances with which glycogen is associated are completely precipitated by mercuric acetate in neutral solution. The well-bruised liver, muscle, or other material is thoroughly extracted with boiling water (addition of acid or alkali serves no useful purpose) and the liquid concentrated by evaporation, mixed with a little potassium acetate and a slight excess of mercuric acetate, filtered, and poured into an equal volume of 85 per cent. alcohol. The precipitated glycogen is purified by repeated solution in water and reprecipitation with alcohol, washed with a mixture of alcohol and ether, and finally dried at 110—120°. Glycogen is thus obtained as a perfectly homogeneous substance having the composition $(C_6H_{10}O_5)_n$. It is not truly soluble in water, since it is more or less completely separated from the liquid by filtration. In the presence of a trace of salts, it is wholly insoluble in 36 per cent. alcohol. Glycogen is not hydrolysed by heating at 100° with 3 per cent. potassium hydroxide solution or with 5 per cent. acetic acid, but when heated with 5—6 per cent. mineral acid at 115—120°, it is converted into a mixture of sugars having a reducing power slightly

greater than that of dextrose. Glycogen from the human liver yields products having a notably higher reducing power than those obtained from rabbit's liver, and from this and other considerations it is concluded that different varieties of glycogen are contained in the different organs of the same animal and also in the same organs of different animals. N. L.

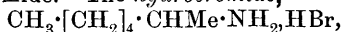
Composition of the Gum of Grevillea Robusta. By RÆSER and PUAUX (*J. Pharm.*, 1899, [vi], 10, 398—400).—The fresh gum is soft, and of a whitish colour, but on keeping it becomes hard, and of a yellowish, and often of a reddish, colour. It is odourless and possesses an astringent taste. It entirely dissolves in water, from which it is precipitated by 95 per cent. alcohol, and by basic lead acetate, after the addition of ammonia, until slightly alkaline. Its aqueous solution reduces Fehling's solution, and when warmed with ferric chloride, its colour deepens, but no precipitate is produced. When the gum is treated with mineral acids, galactose and arabinose are produced. A complete analysis of the gum is given. H. R. LE S.

Nitroacetone. By AD. LUCAS (*Ber.*, 1899, 32, 3179—3182. Compare Abstr., 1899, i, 401 and 433).—When silver nitrite is agitated for 24 hours with a dilute ethereal solution of iodoacetone, the nitroacetone produced remains insoluble, whilst the impurities dissolve; the nitroacetone, separated and dissolved in a larger quantity of ether, crystallises from the concentrated solution in well defined plates, melts at 49° , is soluble in water and alcohol, and crystallises from benzene in needles. Cryoscopic determinations of its molecular weight show that this corresponds with the simple formula $C_3H_5O_3N$. When dissolved in water, it reacts as a monobasic acid, and determinations of its electrical conductivity indicate that its strength is half that of acetic acid, the value of K for nitroacetone being 0.001026. Aminoacetone (Abstr., 1893, 734) is obtained by reducing nitroacetone, and this result indicates that the latter is a nitro-compound and not a nitrite. In aqueous solutions, both nitroacetophenone and nitroacetone behave like isonitroso-derivatives (Hantzsch and Veit, Abstr., 1899, i, 401), but the latter substance does not appear to have any close connection with the compound described as a nitroacetone by Henry (Abstr., 1899, i, 475). When treated with phenylhydrazine, nitroacetone yields an oily *phenylhydrazone*. G. T. M.

γ -Amino- $\beta\beta$ -dimethylbutane. By WASSILY SOLONINA (*Chem. Centr.*, 1899, ii, 474; from *J. Russ. Chem. Soc.*, 1899, 31, 541—542).— γ -Amino- $\beta\beta$ -dimethylbutane, prepared by reducing a boiling alcoholic solution of pinacolone oxime, $CMe_3 \cdot CMe \cdot NOH$, with sodium, is a mobile liquid, has the odour of ammonia, boils at 103 — 104° , and is very slightly soluble in water. At -20° , it forms a crystalline mass. The *hydrochloride* forms long needles, and the *platinichloride* is crystalline; the *aurichloride* crystallises from dilute alcohol in long, pale yellow needles, and melts at 178° . By the action of benzenesulphonic chloride on aminodimethylbutane dissolved in ether, the compound $C_6H_{13} \cdot NH \cdot SO_2Ph$ is formed which crystallises from aqueous alcohol

in thick plates, melts at 96.5° , and is insoluble in water, but easily so in alcohol, ether, or benzene. E. W. W.

β -Heptylamine. By THOMAS CLARKE (*J. Amer. Chem. Soc.*, 1899, 21, 1027—1031. Compare Cahours and Pelouse, *Jahresber.*, 1863, 528; Schorlemmer, *Annalen*, 1863, 127, 318).—When β -heptyl bromide (Abstr., 1881, 82) is heated, with an excess of alcoholic ammonia at 100° , the products are primary β -heptylamine hydrobromide, heptylene, and ammonium bromide. The *hydrobromide*,



crystallises from a mixture of benzene and light petroleum in slender, silky needles melting at 163° , and dissolves readily in alcohol, water, or benzene, and also in large quantities of dry ether. The amine is a slightly brown liquid boiling at 142 — 144° under atmospheric pressure, and of sp. gr. 0.7667 at $24^{\circ}/24^{\circ}$. It dissolves readily in alcohol, ether, or light petroleum, is extremely hygroscopic, and has strongly alkaline properties. The *hydrochloride* crystallises in colourless, silky, somewhat deliquescent needles melting at 133° ; the *platinichloride* crystallises from warm water in large, yellow plates decomposing at 195° ; the *aurichloride* also crystallises in large, yellow plates melting at 63 — 64° , and the *oxalate*, $(\text{C}_7\text{H}_{17}\text{N})_2 \cdot \text{H}_2\text{C}_2\text{O}_4$, in colourless plates which melt and decompose at 204 — 205° , and also decompose when boiled with water. J. J. S.

Behaviour of Diamines on Neutralisation. By MARCELLIN P. E. BERTHELOT (*Compt. rend.*, 1899, 129, 694—700).—The differences observed in the heats of neutralisation for successive equivalents of acid afford a method of distinguishing between monoacid and polyacid bases, and of fixing their molecular weight. The same end is more quickly attained by titrating the base with standard acid and observing the behaviour of different indicators; ethylenediamine and diethylenediamine are thus shown to be monoacid towards phenolphthalein, and diacid towards methyl-orange. Both these bases may be estimated alkalimetrically with considerable accuracy, but the end points are not so delicate with diethylenediamine as with ethylenediamine, a fact which is in harmony with the lower heat of neutralisation of the former base. N. L.

Diamines. Diethylenediamine (Piperazine). By MARCELLIN P. E. BERTHELOT (*Compt. rend.*, 1899, 129, 687—694).—Diethylenediamine hydrate, $\text{C}_4\text{H}_{10}\text{N}_2 \cdot 6\text{H}_2\text{O}$, melts at 44° ; when distilled, a mixture of water and diethylenediamine passes over, the proportion of the latter gradually increasing as the temperature rises until, above 135° , the anhydrous base is obtained. This is a crystalline, tenacious, waxy substance which melts at 104° and dissolves very slowly in water, but is nevertheless very hygroscopic. The heat of dissolution of the base is $+5.16$ Cal. at 14° , and of the hydrate -9.15 Cal. at 16° . The heat of hydration is therefore $+14.31$ Cal. (liquid water) or 4.9 Cal. (solid water). No evidence was found for the existence of more than one hydrate. The heat of combustion of diethylenediamine hydrate is 691.14 Cal. at constant volume, and 691.3 Cal. at constant pressure. The heat of formation of the base

from its elements is 16.6 Cal., and its heat of combustion is calculated as 705.6 Cal.

Comparison of the heat of formation of diethylenediamine with that of ethylenediamine (8.8 Cal.) shows that the conversion of the latter compound into the former, by the fixation of a C_2H_2 group, is accompanied by the development of +7.8 Cal., whereas this transformation, instances of which are cited, is always accompanied by the absorption of heat when the general function of the compound remains unaltered. These facts are in harmony with the view that diethylenediamine is a cyclic compound.

The heat of neutralisation of diethylenediamine is 10.36 Cal. for the first, and 7.05 Cal. for the second, equivalent of hydrochloric acid, all the substances being in solution; diethylenediamine is therefore a weaker base than ethylenediamine, the corresponding figures for which are 12.52 and 11.0 respectively. The heat of dissolution of the hydrated dihydrochloride, $C_4H_{10}N_2 \cdot 2HCl + H_2O$, is +6.0 Cal., and of the anhydrous salt, -4.09 Cal.; the heat of hydration is therefore +1.91 Cal. (liquid water) and +0.3 Cal. (solid water). The heat of formation of the solid anhydrous dihydrochloride from the solid base and the gaseous acid is +61.4 Cal. In the activity of its basic function, diethylenediamine is inferior to ammonia, ethylamine, and methylamine, but superior to aniline.

N. L.

Amic Acids and Imides of Aliphatic Dicarboxylic Acids. By KARL AUWERS [FRITZ MAYER, and F. SCHLEICHER] (*Annalen*, 1899, 309, 316—347).—The author's method for identifying dicarboxylic acids of the aliphatic series (Abstr., 1895, i, 504) meets with certain difficulties (compare Abstr., 1896, i, 639, and 1898, i, 126) which are discussed in the present paper, particularly with regard to the structurally isomeric amic acids of monoalkylsuccinic acids, $CO_2H \cdot CHR \cdot CH_2 \cdot CONHR$ and $CONHR \cdot CHR \cdot CH_2 \cdot CO_2H$, of *as*-dialkylsuccinic acids, and to those *s*-dialkylsuccinic acids which occur in two stereoisomeric forms. It is found that the imides obtained from the structurally isomeric amic acids of monoalkylsuccinic acids by heating them alone, or with acetyl chloride, are identical, and the same remark applies to the amic acids of *as*-dialkylsuccinic acids; when the imides are hydrolysed with alkali, the amic acids produced are either the original ones, their structural isomerides, or mixtures of the two. The following facts in connection with *s*-dialkylsuccinic acids have been ascertained: 1. The fumaroid acid is converted into the fumaroid imide by heating it with a base during a short period, or by heating the fumaroid anilic acid above its melting point; this does not apply to the anil, tolil, and β -naphthil of fumaroid diethylsuccinic acid, because these imides are very labile, and thus become converted into the corresponding maleoid derivatives. 2. Hot acetyl chloride converts the fumaroid anilic acids into the maleoid compounds. 3. Boiling dilute acids convert the fumaroid and maleoid imides into the corresponding fumaroid and maleoid dicarboxylic acids, with a small proportion of the stereoisomeric modifications. 4. Boiling, dilute, aqueous alkalis resolve the anils into the corresponding anilic acids. The *p*-tolil of maleoid

dimethylsuccinic acid yields the maleoid *p*-tolilic acid with aqueous caustic soda, and the fumaroid *p*-tolilic acid with baryta. 5. Alcoholic soda and potash also convert imides into amic acids, but at the same time change the fumaroid compound into the maleoid, the converse taking place to only a slight extent; in some cases, however, the rearrangement does not occur. 6. On the other hand, hot, concentrated aqueous alkalis invariably convert the maleoid amic acids into the fumaric modification; this action is not reversible.

The following melting points are recorded: Methylsuccinic acid *p*-tolilic acid, 164°, *p*-tolil, 109–110°, β -naphthilic acid, 154·5°, β -naphthil, 160·5°. Isopropylsuccinic acid anilic acid, 143°, anil, 91–92°, *p*-tolilic acid, 143–144°, *p*-tolil, 139–140°, β -naphthilic acid, 198°, β -naphthil, 132–132·5°. *as*-Dimethylsuccinic acid anilic acid, 84–86°, *p*-tolil, 113°. Fumaroid *s*-dimethylsuccinic acid *p*-tolilic acid, 194°, *p*-tolil, 120–121°, β -naphthilic acid, 209°; maleoid *s*-dimethylsuccinic acid *p*-tolilic acid, 164°, *p*-tolil, 153°, β -naphthilic acid, 140°, β -naphthil, 220°. Fumaroid *s*-methylethylsuccinic acid anilic acid, 164–165°, anil, 76–77°, *p*-tolilic acid, 175°, *p*-tolil, 87–88·5°, β -naphthilic acid, 191–192°, β -naphthil, 148–150°; maleoid *s*-methylethylsuccinic acid anilic acids, 139–140°, and 100–102°, anil, 103–104°, *p*-tolilic acid, 147–148°, *p*-tolil 109–110°, β -naphthil 159–160°. Fumaroid *s*-diethylsuccinic acid anilic acid, 183–184°, *p*-tolilic acid, 189–190°, β -naphthilic acid, 202–203°, maleoid *s*-diethylsuccinic acid anilic acid, 124–125°, anil, 84–85°, *p*-tolilic acid, 148–149°, *p*-tolil, 92–93°, β -naphthilic acid, 145–146°, β -naphthil, 118–119°. *d*-Camphoranilic acid, 203–204°, *d*-camphoranil, 117–118°; *l*-iso-camphoranilic acid, 183–183·5°. Succinic acid *p*-tolilic acid, 179–180°, *p*-tolylamide, 207° (compare Auwers and Harger, Abstr., 1896, i, 640); dibromosuccinanil, $\begin{array}{c} \text{CHBr}\cdot\text{CO} \\ | \\ \text{CHBr}\cdot\text{CO} \end{array} \text{>NPh}$, prepared from bromine and the anil of maleic acid, 171° (compare Auwers and Singhof, Abstr., 1896, i, 644), chlorosuccinanil, $\begin{array}{c} \text{CH}_2\text{--CO} \\ | \\ \text{CHCl}\cdot\text{CO} \end{array} \text{>NPh}$, 117–118°.

M. O. F.

Methyleneasparagine and Allied Compounds. By Hugo SCHIFF (*Gazzetta*, 1899, 29, ii, 285–303. Compare Abstr., 1899, i, 870).—When exposed to the air, dimethyleneasparagine gives up formaldehyde, the residual substance having a composition corresponding to a *sesquimethyleneasparagine*, $\text{CH}_2(\text{C}_4\text{H}_5\text{O}_3\text{N}_2\cdot\text{CH}_2)_2$; its copper compound has the composition $\text{C}_{11}\text{H}_{14}\text{O}_6\text{N}_4\text{Cu} + \text{H}_2\text{O}$.

Methyleneasparagine acts as a monobasic acid; at 14°, it dissolves in water to the extent of 2·38 per cent., but it is scarcely soluble in alcohol. On allowing its solution in alcoholic hydrochloric acid to evaporate over sulphuric acid, it deposits colourless needles of the hydrochloride of monoethyl aspartate. In aqueous solution, $[\alpha]_D$ has a mean value $-47\cdot58^\circ$; a solution containing methyleneasparagine and potassium hydroxide in molecular proportion gives for potassium methyleneasparaginate $[\alpha]_D - 69\cdot01^\circ$. The presence of a large quantity of water hinders the formation of methyleneasparagine;

on diluting a solution of methyleneasparagine, however, it is not decomposed.

A solution of α -asparagine required for neutralisation 0.63 mol. of potash per mol. of the asparagine, whilst after adding formaldehyde the quantity of potash necessary was increased to 0.95 mol.

The author prefers Piutti's formula, $\text{NH}_2 \cdot \text{CO} \cdot \text{CH}_2 \cdot \text{CMe}(\text{NH}_2) \cdot \text{CO}_2\text{H}$, for homoasparagine, since it resembles β -asparagine in having a feeble acid reaction and in giving an azure-violet biuret reaction.

Methylenehomoasparagine, $\text{NH}_2 \cdot \text{CO} \cdot \text{CH}_2 \cdot \text{CMe}(\text{N} \cdot \text{CH}_2) \cdot \text{CO}_2\text{H} + \text{H}_2\text{O}$, is a colourless, crystalline compound which dissolves readily in water, but only slightly in alcohol, and does not give the biuret reaction. It behaves as a monobasic acid and forms a *copper* compound, $(\text{C}_6\text{H}_9\text{O}_8\text{N}_2)_2\text{Cu}$.

Methyl- α -asparagine gives a reddish-violet biuret reaction, but if formaldehyde is present, no coloration is obtained; it acts as a monobasic acid. Dimethyl- α -asparagine, however, has much feebler acid properties; a concentrated solution neutralises 0.2 mol. of potash per mol. The addition of formaldehyde makes the solution strongly acid again, so that a further 0.6 mol. of potash is required for neutralisation; in the course of an hour, further addition of 0.2 mol. of potash is necessary, the total amount of potash added being 1 mol. for each mol. of the dimethylasparagine. A solution of 1 mol. of dimethylasparagine in 1320 mols. of water, is, however, neutral, but on adding formaldehyde neutralises at once 0.6 mol. of potash, and in the course of the day the remaining 0.4 mol. must be added to keep the solution neutral.

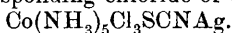
In concentrated aqueous solution, 1 mol. of glutamine neutralises 0.1 to 0.15 mol. of potash; on adding formaldehyde, methyleneglutamine is formed, and acts as a monobasic acid, neutralising a molecular proportion of potash. *Methyleneglutamine* is a colourless, crystalline mass which dissolves readily in water and decomposes carbonates; with copper hydroxide, it forms a dark azure-blue compound apparently very soluble in water.

T. H. P.

Nitrosoalkylurethanes. By ARTHUR HANTZSCH (*Ber.*, 1899, **32**, 3148—3149).—A reply to Brühl (*Abstr.*, 1899, i, 871). T. M. L.

Constitution of Inorganic Compounds. XX. Thiocyanocobalt Salts and Structural Isomerides. By ALFRED WERNER, HERBERT MÜLLER, R. KLIEN, and F. BRÄUNLICH (*Zeit. anorg. Chem.*, 1899, **22**, 91—157).—*Isothiocyanopentammine salts*, $[\text{Co}(\text{NH}_3)_5\text{NCS}]\text{X}_2$, are obtained by the action of potassium thiocyanate on concentrated hot solutions of aquopentammine salts, the sulphate being most advantageously employed; blackish-green additive products of thiocyanic acid and the isothiocyano-salt are formed, but are decomposed on addition of water. The thiocyano-group in these compounds is not dissociated even in dilute aqueous solution, and the characteristic reaction with ferric chloride does not take place. The thiocyano-group is also unaltered by the action of mineral acids, whereby the other acid groups undergo substitution. With silver nitrate, additive compounds of the formula $\text{Co}(\text{NH}_3)_5(\text{NO}_3)_3\text{SCNAg}$ are formed, which, when treated with

hydrochloric acid, do not give a precipitate of silver chloride, but are converted into the corresponding chloride of the formula



Isothiocyanopentamminecobalt sulphate, $[\text{Co}(\text{NH}_3)_5\text{NCS}]\text{SO}_4 + 2\text{H}_2\text{O}$, crystallises in four-sided, thin, yellow plates, and is converted into the hexammine chloride when oxidised with chlorine. The *nitrate*, *chloride*, *bromide*, *iodide*, *platinichloride*, *platinosochloride*, *thiocyanate*, and *nitrite*, obtained by treating the sulphate with the corresponding acids, are also described.

Nitritothiocyanotetramminesalts, $[\text{CoNO}_2(\text{NH}_3)_4\text{SCN}]\text{X}$.—The *chloride* is obtained by the action of potassium thiocyanate on a hot solution of chloronitritotetramminecobalt chloride and subsequent treatment with hydrochloric acid. The thiocyano-group in these compounds is not so firmly combined as in the preceding series, and is gradually completely dissociated in dilute solution; with silver nitrate, similar additive products of the formula $[\text{CoNO}_2(\text{NH}_3)_4\text{SCNAg}]\text{ClNO}_3$ are obtained, which, however, when boiled with water, are decomposed into silver chloride and nitritothiocyanotetramminecobalt nitrate; when shaken with silver oxide, the corresponding base is not obtained, but decomposition takes place with the formation of silver chloride and thiocyanate and the base of the nitrito-aquo-tetrammine series. *Nitritothiocyanotetramminecobalt chloride* crystallises in lustrous leaflets when precipitated from aqueous solution by hydrochloric acid, and in needles and tabular prisms from neutral aqueous solution, is soluble in 33 parts of water, and when oxidised with chlorine yields chloronitritotetrammine chloride. The *bromide*, *iodide*, *thiocyanate*, and *nitrate* are also described.

Dithiocyanodiethylenediaminecobalt salts, $[\text{Co}(\text{C}_2\text{H}_5\text{N}_2)_2(\text{SCN})_2]\text{X}$.—By the action of potassium thiocyanate on dichlorodiethylenediaminecobalt chloride and subsequent evaporation with hydrochloric acid, the chlorides of two isomeric dithiocyanodiethylenediaminecobalt salts are obtained. This isomerism is determined by the isomerism of the dichlorodiethylenediamine salts, since the 1:2-dichlorodiethylenediamine salts (violeo-salts) yield only one dithiocyano-series, the easily soluble salts containing *iso*-thiocyano-groups, whereas 1:6-dichlorodiethylenediamine salts (praseo-series) yield both series of salts and more of the sparingly soluble series, containing thiocyano-groups, as the concentration of the solution to which the potassium thiocyanate is added increases. The easily soluble dithiocyanochloride, when oxidised with chlorine, is converted into diamminediethylenediaminecobalt chloride, that is, the nitrogen atom of the thiocyano-group in direct combination with the cobalt atom is converted into ammonia. The sparingly soluble isomeric chloride, however, when oxidised with chlorine, yields dichlorodiethylenediaminecobalt chloride, in which the thiocyano-group is completely oxidised. As regards the thiocyano-groups, the isomerism is evidently similar to that between the thiocarbimides and the thiocyano-esters. *Diisothiocyanodiethylenediaminecobalt chloride* crystallises, with $1\text{H}_2\text{O}$, in thin, triclinic, ruby-red tablets of rhomboidal habit, and, with $1\frac{1}{2}\text{H}_2\text{O}$, in thick, rhomboidal tablets which appear black in reflected light, is easily soluble in cold water,

yielding a bright ruby-red solution. The *thiocyanate*, *hydrogen sulphate*, *nitrate*, *bromide*, and *iodide* are also described. A normal sulphate cannot be prepared, and this forms a marked distinction between this series and the sparingly soluble series from which only the normal sulphate is obtained.

Dithiocyanodiethylenediaminecobalt chloride crystallises, with $1\text{H}_2\text{O}$, in thin, yellowish-red needles or prisms having a bronze lustre, and in flat, rhomboidal prisms which appear almost black in reflected light, is practically insoluble in cold water, fairly soluble in hot water, and gives a yellowish-red solution. The *thiocyanate*, *sulphate*, *nitrate*, *bromide*, and *iodide* are also described.

Diamminediethylenediaminecobalt chloride, $[\text{Co}(\text{NH}_3)_2(\text{C}_2\text{H}_8\text{N}_2)_2]\text{Cl}_2 + \text{H}_2\text{O}$, obtained by oxidising the above diisothiocyanochloride with chlorine, crystallises in triclinic, many-sided tablets, and in four-sided, yellow pyramids. The aqueous solution is completely precipitated by alcohol, and gives the typical luteo-salt reactions. With cobaltous chloride, similarly to the triethylenediaminecobalt chloride, it yields a *double salt* which crystallises, with $2\text{H}_2\text{O}$, in thin, four-sided plates.

The thiocyano-group is generally combined in the normal manner. In the four series of compounds, thiocyanopentammine salts, nitrothiocyanotetrammine salts, chlorothiocyanodiethylenediamine salts, and oxalothiocyanotriammine salts, only the first series are derivatives of isocyanic acid, since, when oxidised with chlorine, they yield hexammine salts. The remaining salts, when oxidised with chlorine, yield respectively chloronitritotetrammine salts, trichlorodiethylenediamine salts, and oxaloaquotriammine salts. Further, the thiocyano-residues in Reinecke's salt, $\text{Cr}(\text{NH}_3)_2(\text{SCN})_4\text{K}$, and in potassium platinithiocyanate, are completely oxidised and eliminated by chlorine.

The conversion of isothiocyano-group into the ammonia group which remains in direct combination with the cobalt atom, shows that the ammonia molecules in the complex radicle are combined with the metal atom in the same manner as acid groups which are in direct combination with the metal atom. The direct substitution of ammonia by acid groups and the converse substitution cannot be effected, as a rule, in the cobaltammonia compounds. When, however, chloroamminediethylenediaminecobalt chloride is treated with potassium thiocyanate, the ammonia group is replaced by the thiocyano-group, and chlorothiocyanodiethylenediaminecobalt thiocyanate is formed.

Dichlorodiethylenediaminecobalt thiocyanate, $[\text{Co}(\text{C}_2\text{N}_2\text{H}_8)\text{Cl}_2]\text{CNS}$, obtained by adding potassium thiocyanate to an aqueous solution of the diethylenediaminepraseo-chloride, crystallises in small, lustrous, green, six-sided prisms.

Chlorothiocyanodiethylenediaminecobalt thiocyanate,

$$[\text{Co}(\text{C}_2\text{N}_2\text{H}_8)\text{Cl} \cdot \text{SCN}]\text{SCN},$$
 obtained by boiling dichlorodiethylenediaminecobalt chloride with potassium thiocyanate, is a brownish-violet, crystalline powder which, when heated with water, decomposes into the isomeric dithiocyanochlorides, and when evaporated with hydrochloric acid yields the salt $[\text{Co}(\text{C}_2\text{N}_2\text{H}_8)\text{ClSCN}]\text{Cl}$.

E. C. R.

Organo-mercuric Compounds. By GEORGES DENIGÈS (*Ann. Chim. Phys.*, 1899, [vii], 18, 382—432. Compare Abstr., 1895, i, 411; 1898, i, 546, 549, 618; 1899, i, 22, 414, ii, 256).—Citric acid, even when in dilute solution, is readily oxidised by potassium permanganate to acetonedicarboxylic acid; the latter combines readily with mercuric sulphate, forming an insoluble compound (Abstr., 1899, ii, 454); this reaction may be utilised in detecting small quantities of the former acid in the juices of plants, wines, milk, &c. Glycerol, gum, dextrose, sucrose, and acetic, tartaric, malic, succinic, and lactic acids do not interfere with the reaction, but oxalic acid must be removed either by a preliminary oxidation with excess of permanganate or by precipitation as mercuric oxalate.

G. T. M.

Tungsten Alkyls. By EDGAR F. SMITH, E. A. BARNETT, and CLARENCE HALL (*J. Amer. Chem. Soc.*, 1899, 21, 1013—1016).—It has not been found possible to obtain the compound, WMe_3I , described by Riche (*Compt. rend.*, 1856, 42, 203) and by Cahours (*Annalen*, 1862, 122, 70); the authors obtained a black substance, containing over 94 per cent. of tungsten, together with small quantities of carbon and iodine. No tungsten alkyl is obtained when tungsten hexachloride is treated with mercuric ethyl or zinc methyl, nor yet by the action of methyl iodide on tungsten prepared by various methods.

J. J. S.

Cyclic Compounds, Ethylhexanaphthene and Mercuro-heptanaphthene Iodide. By N. KURSANOFF (*Chem. Centr.*, 1899, ii, 477; from *J. Russ. Chem. Soc.*, 1899, 31, 534—535).—By the action of zinc ethyl on chloro- or iodo-naphthene, about 30 per cent. of *ethylnaphthene* is obtained; it boils at 132—133° and has a sp. gr. 0.7913 at 0°/0° and 0.7772 at 20°/0°. A vapour density determination gave 4.04. Naphthylene (cyclohexene), ethylene, ethane, and saturated condensation products boiling at 242—243° under 755 mm. pressure are also formed.

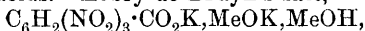
“Mercuro-heptanaphthene iodide,” $\text{C}_6\text{H}_{11}\text{HgI}$, prepared by the action of sodium amalgam on iodo-hexamethylene, crystallises from hot alcohol in lustrous, white scales, melts at 142°, and is decomposed by prolonged heating with liberation of mercuric iodide. E. W. W.

Derivatives of Nitroic Acids. Reactions of Nitro-compounds. By ARTHUR HANTZSCH and HERMANN KISSEL (*Ber.*, 1899, 32, 3137—3148. Compare Abstr., 1899, i, 404).—The names ‘*nitroic acid*’ and ‘*nitroic ester-acid*’ are given to the acids $\text{R}\cdot\text{NO}(\text{OH})_2$ and $\text{R}\cdot\text{NO}(\text{OR}')\cdot\text{OH}$, formed by the addition of water and alcohols to certain nitro-compounds.

Trinitrotoluene potassium methoxide (potassium methyl dinitrotoluene-nitroate), $\text{C}_6\text{H}_2\text{Me}(\text{NO}_2)_2\cdot\text{NO}(\text{OMe})\cdot\text{OK} + \text{H}_2\text{O}$, is a dark violet salt, which explodes when heated; μ_{64} 96.0 and μ_{1024} 113.0, at 25°, showing that the salt is hydrolysed to a considerable extent. The ester-acid, *hydrogen methyl dinitrotoluenenitroate*, is a dark red substance which dissolves only slightly in water or in organic solvents, except acetic acid, in which it has a normal molecular weight; it is a

feeble acid, μ_{1024} 15 at 25° , and is stable in aqueous solution, but evolves nitrous acid when boiled with dilute acids, and gives trinitrotoluene and methyl alcohol when dissolved in concentrated sulphuric acid; it is not attacked by phosphorus pentachloride, and crystallises unchanged from acetic acid, but acetyl chloride converts it into *acetyl methyl dinitrotoluenenitroate*, a microcrystalline substance which explodes on gentle warming, and is hydrolysed by alkalis.

Potassium methyl dinitrobenzenenitroate (trinitrobenzene potassium methoxide) and *potassium methyl dinitroxylenenitroate* (*trinitroxylenepotassium methoxide*) are immediately decolorised by acids, and do not give nitroic ester-acids. Lobry de Bruyn's salt,



gives an unstable *nitroic ester-acid*, from which trinitrobenzoic acid is regenerated on evaporating the solution.

p-Nitrobenzylnitramine (Hantzsch and Hilland, *Ber.*, 31, 2058) interacts with 2 mols. sodium ethoxide to form the *sodium ethyl nitroate*, $\text{N}_2\text{O}_2\text{Na} \cdot \text{CH}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{NO}(\text{OEt}) \cdot \text{ONa}$, a deep-red, soluble salt which decomposes in moist air, cannot be recrystallised, and sometimes inflames spontaneously in the desiccator. The *ester-acid* is also extremely unstable, and changes quickly into a yellow resin, from which *p*-nitrobenzoic acid was obtained.

Sodium trinitrobenzoate combines, at least partially, in solution with another molecule of sodium hydroxide to form a *sodium nitroate*, which could not be isolated, but was shown to be present by the conductivity and colour of the solution. *Barium dinitrobenzonitroate*, $\left[\text{Ba} \begin{array}{c} \diagup \text{O} \diagdown \\ \diagdown \text{O} \diagup \end{array} \text{NO} \cdot \text{C}_6\text{H}_2(\text{NO}_2)_2 \cdot \text{CO}_2 \right]_2 \text{Ba}$, prepared by the action of barium

hydroxide on trinitrobenzoic acid, is a dark, brownish-red salt, very slightly soluble in water, and very explosive; the nitroic acid is unstable. Trinitrobenzene and trinitrotoluene dissolve in caustic alkalis, giving deep red solutions, but the formation of nitroates appears to be only very partial; on acidifying the alkaline solutions at 0° , red solutions are obtained which appear to contain the nitroic acids, but these are unstable at the ordinary temperature.

Hepp's trinitrobenzene potassium cyanide (*Annalen*, 1883, 215, 360), to which the formula $\text{C}_6\text{H}_3(\text{NO}_2)_2 \cdot \text{NO}(\text{CN}) \cdot \text{OK}$ is assigned, is a deep-violet, crystalline, explosive salt; *dinitrobenzenecyanonitroic acid* (*trinitrobenzene cyanhydrin*), which is precipitated by mineral acids from a solution of the potassium salt, crystallises from ether or benzene in red needles, and decomposes at 175° ; it is not acted on by phosphorus pentachloride or acetyl chloride.

The characteristic reactions of the nitro-paraffins are shown to be really those of the isonitro-compounds. Nitroethane is scarcely attacked by bromine in aqueous solution, but a solution of isonitroethane, freshly prepared at 0° by the action of hydrochloric acid on the sodium salt, brominates completely and smoothly. A solution of nitroethane gives no nitrolic acid with nitrous acid, but isonitroethane interacts readily with it. Isonitroethane and diazonium hydroxide interact immediately at 0° , whilst true nitroethane is inactive; similarly, phenylisonitromethane interacts readily with diazonium hydroxide and isonitroethane with *p*-bromodiazonium hydroxide. The conclu-

sion is drawn that the true nitro-compounds are, of themselves, no more active than the corresponding halogen compounds, and owe their apparent chemical activity entirely to the formation of the labile isonitro-compounds, and not to the negative character of the $-\text{NO}_2$ group. T. M. L.

Transformation of Styrene into Metastyrene under the Influence of Light. By GEORGES LEMOINE (*Compt. rend.*, 1899, 129, 719—722. Compare Abstr., 1898, i, 70).—The polymerisation of styrene is effected by the action of heat in the dark, and also under the influence of sunlight at the ordinary temperature; in the latter case, the action is slower, 1—3 per cent. of the substance being transformed in an hour. In this change, the blue and ultra-violet rays are principally concerned; their activity does not extend much below a depth of 4 mm., and is greatly decreased by cooling the insolated liquid; the action does not continue after removal from the influence of light, or only to a very small extent. The velocity of transformation in the light is approximately equal to that observed in the dark at a temperature 50° higher. The general conclusion arrived at is that, in the conversion of styrene into metastyrene, light exerts an accelerating action on an exothermic transformation which takes place in the dark at the same temperature, although more slowly.

N. L.

Naphthalene-1:3:5-trisulphonic Acid. By HUGO ERDMANN (*Ber.*, 1899, 32, 3186—3191. Compare Armstrong and Wynne, *Proc.*, 1887, 146, and 1893, 166).—Polysulphonic acids containing two or three sulphonic groups in β -positions are obtained when naphthalene is sulphonated with fuming sulphuric acid at high temperatures; of these, the 1:3:6-trisulphonic acid, recognised by its sodium and lead salts and its chloride, is the chief product (*Proc.*, 1887, 146).

Naphthalene-1:3:5-trisulphonic acid, the original product of sulphonation, is only obtained when the whole of the reaction is carried out below 90° . Sodium naphthalene-1:5-disulphonate is mixed with fuming sulphuric acid at 50° , and the reaction completed at 90° ; the 1:3:5-acid which is thus produced is separated in the form of its sodium salt; this compound is converted into the sulphonic chloride (m. p. $145\text{--}148^\circ$), which is then boiled with methyl alcohol, and the solution evaporated to dryness; in this way, the acid is obtained as a colourless syrup.

Naphthalene-1:3:5-trisulphonic acid resembles the non-volatile mineral acids; it is very hygroscopic, destroys cellulose with liberation of carbon, and decomposes sodium chloride.

The *aniline* salt, $\text{C}_{10}\text{H}_5(\text{SO}_3\text{H})_3 \cdot 3\text{NH}_2\text{Ph}$, produced by adding aniline to an aqueous solution of the acid, or by double decomposition from aniline hydrochloride and sodium naphthalenetrisulphonate, crystallises from water in aggregates of white, silky needles. The salt is not hygroscopic, and is readily soluble in water, but less so in brine solution. The *p-toluidine* salt is more soluble than the aniline compound; the benzidine salt, $2\text{C}_{10}\text{H}_5(\text{SO}_3\text{H})_3 \cdot 3\text{C}_{12}\text{H}_8(\text{NH}_2)_2$, crystal-

lises with $4\text{H}_2\text{O}$, and the dianisidine salt separates slowly from its solution in glacial acetic acid in short, hard needles. G. T. M.

Polymerisation of Inorganic Chloroanhydrides. II. By GIUSEPPE ODDO (*Gazzetta*, 1899, 29, ii, 330—343. Compare also this vol., ii, 74).—The products obtained on heating phosphorus pentachloride and oxychloride, in a reflux apparatus, with varying quantities of water are as follows: With $2\text{PCl}_5 + \text{H}_2\text{O}$, half of the pentachloride is converted into oxychloride, the rest being unchanged; $2\text{PCl}_5 + 2\text{H}_2\text{O}$ yields the theoretical amount of oxychloride; $2\text{PCl}_5 + 3\text{H}_2\text{O}$ or $(\text{POCl}_3)_2 + \text{H}_2\text{O}$ gives mainly oxychloride accompanied by a little pyrophosphoryl chloride, $\text{P}_2\text{O}_3\text{Cl}_4$, and phosphoric oxide; with the proportions $2\text{PCl}_5 + 4\text{H}_2\text{O}$ or $(\text{POCl}_3)_2 + 2\text{H}_2\text{O}$, the same products as in the previous case are obtained, the amount of oxychloride being considerably diminished, and that of phosphoric oxide correspondingly increased.

The interaction of phosphorus pentachloride (3 mols.) on phosphoric oxide (1 mol.), yields a little oxychloride and a considerable quantity of pyrophosphoryl chloride, and is recommended as a good method for preparing the latter.

Potassium chlorate reacts with phosphorus oxychloride according to the equation $(\text{POCl}_3)_2 + \text{KClO}_3 = \text{P}_2\text{O}_5 + \text{KCl} + 3\text{Cl}_2$. This reaction offers a convenient method of chlorination where a definite quantity of chlorine is required.

By heating together phosphorus oxychloride and aniline hydrochloride in molecular proportions in a reflux apparatus, hydrogen chloride is evolved and dichlorophosphoxymonoanilide, $\text{NHPh} \cdot \text{POCl}_2$, obtained. The molecular weight of the latter in boiling benzene varies from 215 with a concentration 0.7944 to 276 when the concentration is 5.2183; using the same solvent, the numbers given by the cryoscopic method are 221 (concentration 0.9676) and 252 (concentration 1.8323). The calculated value is 210. Michaelis and Schulze (*Abstr.*, 1894, i, 128) state that this compound distils in a vacuum with partial decomposition; the author finds, however, that at 90° evolution of hydrogen chloride commences, and at 180° continues until 1 mol. HCl is lost per molecule of the substance, the residue being a new compound to be described later.

Using three mols. of aniline hydrochloride to one of phosphorus oxychloride, two products are obtained. The first, monochlorophosphoxydianilide, $\text{POCl}(\text{PhNH})_2$, gives, in boiling alcohol, a molecular weight varying from 270 with a concentration of 1.3856 to 184 when the concentration is 3.6192; the molecular weight falls if the boiling be prolonged. These observations are at variance with those of Michaelis and Schulze (*Abstr.*, 1894, i, 588). The other product is oxyphosphoazobenzeneanilide, melting at $320\text{--}325^\circ$, and not at 357° as stated by Michaelis and Silberstein (*Abstr.*, 1896, i, 344).

If six molecular proportions of a benzene solution of aniline be treated with one of phosphorus oxychloride, the trianilide of orthophosphoric acid, $\text{PO}(\text{PhNH})_3$, is obtained; its molecular weight in boiling alcohol is 358—359, the calculated value being 323.

The action of phosphorus oxychloride on phenol yields the compound $\text{POCl}_2 \cdot \text{OPh}$, which gives the normal molecular weight in boiling benzene, a little of the chloride $\text{POCl}(\text{OPh})_2$, triphenyl phosphate, which in boiling benzene has the normal molecular weight, and a little diphenylphosphinic acid. T. H. P.

Salicylanilinoacetic Acid [*o*-Carboxyphenylglycollic Acid Monanilide] and its Derivatives. By GEORG COHN (*J. pr. Chem.*, 1899, [ii], 60, 404—406).—The *monanilide* of *o*-carboxyphenylglycollic acid, $\text{NHPh} \cdot \text{CO} \cdot \text{C}_6\text{H}_4 \cdot \text{O} \cdot \text{CH}_2 \cdot \text{CO}_2\text{H}$, prepared by the action of chloroacetic acid on salicylaniline, separates from alcohol, in which it is readily soluble, in white needles melting at 159° .

The corresponding *phenetidide* crystallises from methyl alcohol, in which it is sparingly soluble, in rhombic leaflets melting at 175 — 178° .

The *anisidine* compound, $\text{OMe} \cdot \text{C}_6\text{H}_4 \cdot \text{NH} \cdot \text{CO} \cdot \text{C}_6\text{H}_4 \cdot \text{O} \cdot \text{CH}_2 \cdot \text{CO}_2\text{H}$, crystallises from methyl alcohol in bundles of long needles and melts indefinitely at 174° . A. L.

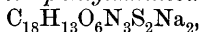
Diphenylamine Derivatives, especially Sulphonic Acids. By ROBERT GNEHM and H. WERDENBERG (*Zeit. angew. Chem.*, 1899, 1027—1030, 1051—1055, and 1128. Compare Merz and Weith, this Journ., 1873, 74).—Sulphuric acid of 66° Bé. does not react with diphenylamine in the cold, and even on warming at 100 — 150° the chief sulphonation product is the disulphonic acid, although a considerable quantity of the base remains unaltered; the chief and, in some cases, the only product formed when concentrated sulphuric acid is employed, at temperatures between 105° and 140° , is the disulphonic acid. Fuming sulphuric acid of different strengths at 50° yields a mixture of mono- and di-sulphonic acids which it is impossible to separate. In all the experiments made, the unaltered diphenylamine was found to contain a substance soluble in ether and melting at 246 — 248° .

Diphenylaminesulphonic acid is most readily obtained by sulphonating acetyldiphenylamine with fuming sulphuric acid (10—25 per cent. anhydride) and subsequently hydrolysing. In the sulphonation, it is advisable to add phosphoric oxide in order to hinder hydrolysis by the water formed.

Barium acetyldiphenylamine sulphonate, $\text{C}_{28}\text{H}_{24}\text{O}_8\text{N}_2\text{S}_2\text{Ba}$, is extremely hygroscopic, and could not be obtained in a crystalline condition. For the preparation of diphenylaminesulphonic acid, it is not necessary to isolate the pure acetyl derivative; the crude sulphonic mixture may be boiled with water for some 3 hours and then treated with barium carbonate. *Barium diphenylaminesulphonate*, $\text{C}_{24}\text{H}_{20}\text{O}_6\text{N}_2\text{S}_2\text{Ba}$, is very sparingly soluble in cold water, and crystallises in snow-white, anhydrous, glistening plates which do not decompose at 170° . The *copper* salt, with $2\text{H}_2\text{O}$, and the *sodium* salt were also prepared. Diphenylaminesulphonic acid condenses with formaldehyde in aqueous acid solution, yielding *trianilinotriphenylmethanesulphonic acid*, $\text{C}_{19}\text{H}_{31}\text{O}_9\text{N}_3\text{S}_3$, which dissolves in water or alcohol, readily undergoes oxidation in solution, and turns pale blue on exposure to the air.

Diphenylaminesulphonic acid is best prepared from the copper salt ; it crystallises in colourless plates, is readily soluble in alcohol or water, and condenses with diazonium solutions, yielding acid dyes.

Sodium p-sulphobenzeneazodiphenylaminesulphonate,



crystallises from hot water in violet plates and dyes silk or wool orange-yellow.

Sodium hydroxydinitrobenzeneazodiphenylaminesulphonate, $\text{C}_{18}\text{H}_{12}\text{O}_8\text{N}_3\text{SNa}$, forms glistening, brown plates. Diphenylaminesulphonic acid (2 mols.) forms a salt with picramic acid (1 mol.).

Acetyldi-p-nitrodiphenylamine, $\text{NAc}(\text{C}_6\text{H}_4\cdot\text{NO}_2)_2$, obtained when acetyldiphenylamine is treated with a mixture of sulphuric and nitric acids at $8-15^\circ$, crystallises from hot alcohol in pale yellow, glistening plates melting at 164° and readily soluble in most organic solvents ; when warmed with concentrated hydrochloric acid, it yields di-p-nitrodiphenylamine.

When barium acetyldiphenylaminesulphonate is nitrated with a mixture of fuming sulphuric (5 per cent. anhydride) and fuming nitric acids, first at 15° and then at $30-35^\circ$, a nitro-derivative is formed the barium salt of which could not be obtained in a crystalline condition, but when hydrolysed with sulphuric acid (37 per cent.), *nitrodiphenylaminesulphonic acid* was obtained, the *barium* salt of which is readily soluble in water and forms dark red crystals. The acid has not been obtained in a pure form and is probably a mixture of ortho- and para-nitro-compounds.

Barium diphenylaminesulphonate is much more readily nitrated than its acetyl derivative, the most suitable reagent being a mixture of concentrated nitric and sulphuric acids at 0° . The product is a *mononitro-derivative*.

Barium diphenylaminedisulphonate separates from water in crystalline masses containing $2\text{H}_2\text{O}$; the *potassium* salt contains $1\frac{1}{2}\text{H}_2\text{O}$ and the *copper* salt $4\text{H}_2\text{O}$; the *acid* is readily soluble in water or alcohol, and has only been obtained in the form of a syrup. When the barium salt is nitrated with a mixture of nitric acid of sp. gr. 1.4 and concentrated sulphuric acid, the product is a *mononitro-derivative*, the *barium* salt of which, $\text{C}_{12}\text{H}_8\text{O}_8\text{N}_2\text{S}_2\text{Ba} + 2\text{H}_2\text{O}$, forms indefinite, orange-red crystals readily soluble in warm water ; the *potassium* salt contains $1\frac{1}{2}\text{H}_2\text{O}$. When reduced by Claisen's method (*Ber.*, 1879, 12, 1946), *aminodiphenylaminedisulphonic acid* is obtained, the *barium* salt of which, $\text{C}_{12}\text{H}_{10}\text{O}_6\text{N}_2\text{S}_2\text{Ba}$, forms a reddish-coloured mass, readily soluble in water, but insoluble in alcohol. J. J. S.

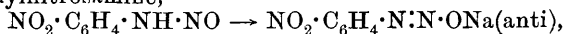
Characterisation of Weak Acids and Pseudo-acids. By ARTHUR HANTZSCH (*Ber.*, 1899, 32, 3066—3088. Compare *Abstr.*, 1899, i, 399).—It is well known that the molecular conductivity, μ , of the sodium salt of a comparatively strong acid increases with the dilution, and that the increase consequent on a doubling of the dilution has a diminishing value, tending towards 0 ; further, that the increase consequent upon a change of dilution from 32 to 1024 litres per gram-mol. ($\Delta_{1024-32}$) has a value of 10—12 ; also, the sodium salts of such acids are neutral to litmus (or to a solution of potassium iodide and iodate), and are not hydrolysed appreciably in aqueous solu-

tion. Strong acids, moreover, combine with dry ammonia, both directly and when dissolved in non-dissociating media, such as benzene. In the case of very weak acids, the sodium salts are more or less hydrolysed; a certain amount of sodium hydroxide is present in the aqueous solution, which then has an alkaline reaction to litmus, and exhibits an increasing, instead of a decreasing, rate of increase of conductivity with dilution, and a resulting abnormally high value of $\Delta_{1024-32}$ (regard must be had to the fact that the alkalinity may be due, as in the case of diazotates, to a little alkali from which it is practicably impossible to free the salt). These regularities were investigated in the case of some weak, or very weak, acids, and the results are tabulated below: K is the value of the dissociation constant of the acid; and the percentage of the sodium salt hydrolysed in an aqueous solution containing 1 gram-mol. in 32 litres (V_{32}) was determined approximately by measuring the hydrolysing effect upon methyl acetate (compare Shields, Abstr., 1893, ii, 448):

	K at 25°.	$\Delta_{1024-32}$.	Sodium salt. Per cent. hydro- lysed (V_{32}).
Phenol	5×10^{-7}	28.0	6
<i>o</i> -Chlorophenol	—	16.7	2.1
2:4-Dichlorophenol	31 „	11.9	0.52
<i>p</i> -Cyanophenol	61 „	11.7	0.52
2:4:6-Trichlorophenol...	1000 „	—	0.37
<i>p</i> -Nitrophenol	96 „	11.9	0.28

It is noticeable that, although nitrophenol, $\text{OH} \cdot \text{C}_6\text{H}_4 \cdot \text{NO}_2$, is 10 times as weak an acid as trichlorophenol, yet its sodium salt is less hydrolysed; this salt must therefore be derived from an acid stronger than trichlorophenol, such as $\text{O} \cdot \text{C}_6\text{H}_4 \cdot \text{NO} \cdot \text{OH}$, and nitrophenol must be regarded in consequence as a pseudo-acid.

The following rules are given for use in the diagnosis of pseudo-acids. I. *The substance is neutral.* (1) The salt is neutral (therefore not hydrolysed, and so the salt of a strong acid): the substance is a pseudo-acid; for instance, phenylnitromethane, $\text{CH}_2\text{Ph} \cdot \text{NO}_2 \rightarrow \text{CHPh} \cdot \text{NO} \cdot \text{ONa}$. (2) The salt is alkaline: if $\Delta_{1024-32}$ is not greater than 12—13 (or if the hydrolysis is small): the substance is a pseudo-acid; for instance, quinonehydrazone, $\text{NHPh} \cdot \text{N} \cdot \text{C}_6\text{H}_4 \cdot \text{O} \rightarrow \text{NPh} \cdot \text{N} \cdot \text{C}_6\text{H}_4 \cdot \text{ONa}$, and isonitrosoacetone, $\text{NOH} \cdot \text{CH} \cdot \text{CMeO} \rightarrow \text{NO} \cdot \text{CH} \cdot \text{CMe} \cdot \text{ONa} (?)$. II. *The substance is feebly, or very feebly acid.* (1) The salt is neutral: the substance is a pseudo-acid; for instance, nitrophenylnitrosamine,

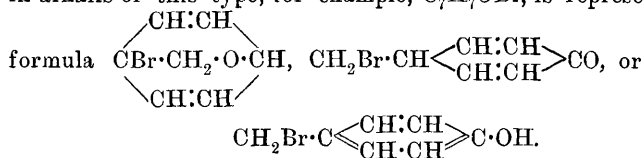


ethylnitrolic acid, $\text{CMe} \begin{smallmatrix} \text{NO}_2 \\ \text{NOH} \end{smallmatrix} \rightarrow \text{CMe} \begin{smallmatrix} \text{N} \\ \text{NO}(\text{ONa}) \end{smallmatrix} \text{O}$, and dinitro-

ethane, $\text{NO}_2 \cdot \text{CHMe} \cdot \text{NO}_2 \rightarrow \text{NO}_2 \cdot \text{CMe} \cdot \text{NO} \cdot \text{ONa}$. (2) The salt is alkaline: if $\Delta_{1024-32}$ is but slightly greater than the normal value, the substance is a pseudo-acid; for instance, *p*-bromophenylnitrosamine, $\text{C}_6\text{H}_4\text{Br} \cdot \text{NH} \cdot \text{NO} \rightarrow \text{C}_6\text{H}_4\text{Br} \cdot \text{N} \cdot \text{N} \cdot \text{ONa}$; if $\Delta_{1024-32}$ is decidedly greater than the normal value, the percentage of hydrolysis must be determined: if this is much less than that of sodium

phenoxide, the substance is a pseudo-acid; in the opposite case, nothing can be predicated, and other properties must be taken into account. III. *The substance is a pronounced acid* with a dissociation constant readily susceptible of measurement; the salt is not perceptibly hydrolysed: the substance, at any rate the ionised part of it, has the same constitution as the ionised salt; it is possible that the undissociated substance may have a different constitution, when the case would be one of 'ionisation isomerism.' C. F. B.

Bromophenols Insoluble in Alkalis. By KARL AUWERS (*Ber.*, 1899, 32, 2978—2987. Compare Abstr., 1898, i, 70 and 646).—A further discussion of the formulæ of these bromophenols. At present, it is impossible to decide whether a compound insoluble in alkalis of this type, for example, C_7H_7OBr , is represented by the



R. H. P.

Bromophenols from *as-o*-Xylenol and *as-m*-Xylenol. By KARL AUWERS (*Ber.*, 1899, 32, 2987—3005).—A comparison of the properties of the compounds described in the following three abstracts.

R. H. P.

Pentabromide from [Pentabromo-derivative of] *as-m*-Xylenol. By KARL AUWERS and W. HAMPE (*Ber.*, 1899, 32, 3005—3016. Compare Abstr., 1896, i, 424, and 1897, i, 33).—The acetyl derivative of $\omega\omega:2:5:6$ -pentabromo-1:3:4-xylenol, $C_6Br_3(CH_2Br)_2 \cdot OAc$ (Zincke, Abstr., 1898, i, 70), forms colourless needles melting at 180° , and is easily reduced to the *acetyl* derivative of tribromo-1:3:4-xylenol, which crystallises from glacial acetic acid in lustrous prisms melting at 115 — 116° .

$\omega\omega$ -*Diiodotribromo*-1:3:4-xylenol, $C_6Br_3(CH_2I)_2 \cdot OH$, prepared from the corresponding diacetate (m. p. 172° , *loc. cit.*) by treatment with hydrogen iodide, crystallises from glacial acetic acid in rosettes of small needles which melt at 182 — 183° , and undergo gradual decomposition without previous solution when treated with aqueous alkalis. The same diacetate, on treatment with an excess of alkali, yields an insoluble, amorphous powder, the constitution of which could not be determined; on treatment with acetone, it yields a *substance* which melts at 230 — 232° , and is probably the acetyl derivative of tribromo-4-hydroxy-*m*-xylylene glycol, $OH \cdot C_6Br_3(CH_2 \cdot OH) \cdot CH_2 \cdot OAc$.

The *glycol*, obtained by treating the dibromide with acetone and water, crystallises from benzene in slender needles melting at 145 — 146° , and yields a *trimethyl ether* melting at 95 — 96° , which, when treated with hydrogen bromide, yields *pentabromo*-1:3:4-xylenol *methyl ether*, $C_6Br_3(CH_2Br)_2 \cdot OMe$, melting at 165 — 168° .

Pentabromo-1:3:4-xylenol, when treated with aniline in benzene solution, yields a $\omega\omega$ -*dianilide*, which is a yellow, crystalline powder

melting at 118—121°. If the acetyl derivative of the pentabromo-compound is used, a *monoacetyl* derivative of the dianilide is obtained; it melts at 209°, is soluble in alkalis, and when boiled with acetic anhydride yields a *diacetate* insoluble in alkalis and melting at 116—118°. The *dipiperidide*, obtained in a similar manner, is a colourless, crystalline powder melting at 115—117°, and yields bromanil on oxidation with nitric acid. The diacetate (m. p. 172°), when oxidised in similar manner, yields a *tetrabromotoluquinone*, $\text{CBr} \begin{smallmatrix} \diagup \text{CO} \cdot \text{CBr} \\ \diagdown \text{CBr} \cdot \text{CO} \end{smallmatrix} \text{C} \cdot \text{CH}_2 \cdot \text{Br}$, which crystallises in yellow, lustrous leaflets melting at 258—259°, and on reduction yields the corresponding *quinol*, which forms brownish needles melting at 226—227°. R. H. P.

Pentabromo-derivative of *as-o*-Xylenol. By KARL AUWERS and R. VON ERGGELET [and in part H. VAN DE ROVAART and W. WOLFF] (*Ber.*, 1899, 32, 3016—3033).— $\omega : 3 : 5 : 6$ -*Pentabromo-1 : 2 : 4-xylenol*, $\text{C}_6\text{Br}_3(\text{CH}_2\text{Br})_2 \cdot \text{OH}$, obtained by heating tribromo-1 : 2 : 4-xylenol with an excess of bromine in a sealed tube at 130°, crystallises from glacial acetic acid in lustrous needles melting at 149—150°, and is insoluble in alkalis. The *acetyl* derivative melts at 127—128°, and is only slowly decomposed by boiling alkalis; on reduction, it yields the *acetyl* derivative of tribromo-1 : 2 : 4-xylenol (m. p. 111—112°). $\omega : 3 : 5 : 6$ -*Tetrabromo-1 : 2 : 4-xylenol- ω -methyl ether*, $\text{OH} \cdot \text{C}_6\text{Br}_3(\text{CH}_2\text{Br}) \cdot \text{CH}_2 \cdot \text{OMe}$, formed when the pentabromo-compound is boiled with methyl alcohol, melts at 132—133°, and is soluble in caustic soda solution. The *monoacetyl* derivative melts indefinitely between 80° and 90° and, if treated with sodium acetate and acetic anhydride, yields the *diacetate*, $\text{OAc} \cdot \text{C}_6\text{Br}_3(\text{CH}_2 \cdot \text{OAc}) \cdot \text{CH}_2 \cdot \text{OMe}$, melting at 101—102°. The corresponding *ethyl ether* forms sharp-angled prisms melting at 124—125°, and yields a similar *diacetate* melting at 105—107°.

$\omega : 2 : 5 : 6$ -*Tetrabromo-1 : 2 : 4-xylenol*, $\text{OH} \cdot \text{C}_6\text{Br}_3(\text{CH}_2\text{Br}) \cdot \text{CH}_2 \cdot \text{OH}$, prepared by treating the pentabromo-compound with acetone and water, crystallises from benzene in needles melting at 166—167°, and is soluble in alkalis. A poor yield of the corresponding *glycol* melting at 185° is obtained after further treatment with acetone. Its *dimethyl ether*, $\text{OH} \cdot \text{C}_6\text{Br}_3(\text{CH}_2 \cdot \text{OMe})_2$, is a colourless, crystalline powder melting at 157°. The *diethyl ether*, obtained by treating the monoethyl ether of the tetrabromo-xylenol with alcohol, crystallises in the form of compact prisms and cubes melting at 94°. The *triethyl ether* is a thick oil, which, on treatment with hydrogen bromide, yields *pentabromo-1 : 2 : 4-xylenol ethyl ether*, $\text{C}_6\text{Br}_3(\text{CH}_2\text{Br})_2 \cdot \text{OEt}$, in the form of needles melting at 108—114°. The pentabromo-compound, on treatment with sodium acetate and acetic acid, yields the *monoacetyl* derivative, $\text{OH} \cdot \text{C}_6\text{Br}_3(\text{CH}_2\text{Br}) \cdot \text{CH}_2 \cdot \text{OAc}$, which crystallises in needles melting at 154—155°, forms a phenylurethane melting at 193°, and when boiled with alcohol yields an *ethyl ether*,

$\text{OH} \cdot \text{C}_6\text{Br}_3(\text{CH}_2\text{Br}) \cdot \text{CH}_2 \cdot \text{OEt}$, melting at 124—125°. The *diacetyl* derivative of the tetrabromo-compound forms small needles melting at 116°, and on treatment with

acetic anhydride yields the *triacetyl* derivative, $\text{OAc} \cdot \text{C}_6\text{Br}_3(\text{CH}_2 \cdot \text{OAc})_2$, melting at $133\text{--}134^\circ$.

On treatment with *o*-toluidine, the pentabromo-compound is converted into the *di-o-toluidide* which melts at 153° and forms an *ethyl ether* melting at $121\text{--}123^\circ$.

The tetrabromo-compound, when treated with aniline in benzene solution, yields the *compound* $\text{OH} \cdot \text{C}_6\text{Br}_3(\text{CH}_2 \cdot \text{OH}) \cdot \text{CH}_2 \cdot \text{NHPh}$, which melts at 171° and forms a triacetyl derivative melting and decomposing at $179\text{--}181^\circ$.

ω-Diiodotribromo-1:2:4-xyleneol, prepared by treating the tetrabromo-compound previously described with hydrogen iodide, forms yellowish, compact crystals melting at $165\text{--}166^\circ$, and yields a *monoacetyl* derivative melting at 142° . On treatment with acetone, this diiodo-compound forms a *monoiodo*-derivative melting at 193° , the *diethyl ether* of which melts at $110\text{--}111^\circ$. The diiodo-compound, when treated with glacial acetic acid and sodium acetate, yields the *monoacetyl* derivative of the monoiodo-compound which melts at $185\text{--}190^\circ$. On reduction, the tetrabromo-xyleneol yields the *alcohol*, $\text{OH} \cdot \text{CH}_2 \cdot \text{C}_6\text{MeBr}_3 \cdot \text{OH}$ [$= 1:2:4$]. This crystallises from benzene as silky needles melting at $170\text{--}180^\circ$, and yields a *diacetate* melting at $135\text{--}137^\circ$. The *monoacetyl* derivative, $\text{OH} \cdot \text{C}_6\text{MeBr}_3 \cdot \text{CH}_2 \cdot \text{OAc}$, melts at $140\text{--}142^\circ$. On oxidation of the alcohol with nitric acid, tribromotoluquinone is obtained in the form of yellowish leaflets melting at $233\text{--}235^\circ$.

R. H. P.

Heptabromo-derivative of *as-o*-Xyleneol. By KARL AUWERS and HARRY BURROWS [and in part H. VAN DE ROYAART] (*Ber.*, 1899, **32**, 3034—3045).—*ωωωω*:3:4:6-*Heptabromo-1:2:4-xyleneol*, $\text{OH} \cdot \text{C}_6\text{Br}_3(\text{CHBr}_2)_2$, prepared by heating tribromo-1:2:4-xyleneol in a sealed tube at 190° with an excess of bromine, forms light, silver-grey crystals melting at 199° , and is insoluble in alkalis. The *acetyl* derivative melts at 193° , and is easily reduced to acetyltribromo-1:2:4-xyleneol. On boiling the heptabromo-derivative with methyl alcohol, the *dimethylacetal*, $\text{CH}(\text{OMe})_2 \cdot \text{C}_6\text{Br}_3(\text{CHBr}_2) \cdot \text{OH}$ [$= 1:2:4$], melting at $116\text{--}118^\circ$, is formed. The corresponding *diethyl acetal* melts at 143° . The corresponding *diacetate*, formed by treating the heptabromoxyleneol with glacial acetic acid and sodium acetate, crystallises in colourless plates melting at 155° , and when boiled with acetic anhydride yields the *triacetyl* compound, $\text{OAc} \cdot \text{C}_6\text{Br}_3(\text{CHBr}_2) \cdot \text{CH}(\text{OAc})_2$, melting at $132\text{--}133^\circ$. When the acetals just described are warmed with glacial acetic acid, *ωω*:3:4:6-*pentabromo-5-hydroxy-o-tolualdehyde* is obtained; it crystallises in small needles melting at 168° , is soluble in alkalis, and forms an *acetyl* derivative melting at 150° . On oxidation with nitric acid, it yields *pentabromotoluquinone*, $\text{CHBr}_2 \cdot \text{CBr}_3\text{O}_2$, which crystallises from glacial acetic acid in yellow prisms melting at 160° . 3:4:6-*Tribromo-5-hydroxy-o-tolualdehyde*, obtained by the reduction of the pentabromo-compound, forms small needles melting at $187\text{--}188^\circ$, and yields a *benzoyl* derivative melting at $167\text{--}168^\circ$ and an *oxime* melting at 207° ; on oxidation, it yields *tribromotoluquinone* melting at 234° . Attempts were made to synthesise this aldehyde by brominating *p*-hydroxy-*o*-tolualdehyde. In this way,

4:6-dibromo-3-hydroxy-o-tolualdehyde is obtained; it forms small needles melting at 161—162°, yields an *oxime* melting at 197°, and is oxidised to 4:6-dibromo-3-hydroxy-o-toluic acid, which forms small, white needles melting at 232°. On further treatment with bromine, this aldehyde is converted into tetrabromo-*m*-cresol. This can also be prepared by the direct bromination of *m*-cresol or of *as*-o-xylene; it forms long, thin needles melting at 194°, is easily soluble in alkalis, and forms an *acetyl* derivative melting at 165—166°, and a *benzoyl* derivative melting at 153—154°; when treated with nitric acid, it yields tribromotoluquinone and an unstable *mononitro*-derivative melting at 88°.

Tribromo-p-hydroxyphthalaldehyde, $\text{OH} \cdot \text{C}_6\text{Br}_3(\text{COH})_2$, prepared by treating pentabromohydroxytolualdehyde with lime water, crystallises from dilute alcohol in the form of colourless needles and prisms melting at 202°, and yields an *acetyl* derivative melting at 205—209°. An isomeric substance melting at 245—247°, and forming an *acetyl* derivative melting at 218—220°, is obtained in small quantity in the preparation of this hydroxyphthalaldehyde. R. H. P.

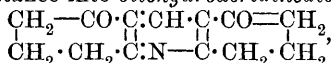
Catechol Derivatives. By CHARLES MOUREU (*Ann. Chim. Phys.*, 1899, [vii], 18, 76—139).—An account of work already published. (Compare Abstr., 1896, i, 215, 426, 477, 646; 1897, i, 336, 403; 1898, i, 411, 518, 644, 660; 1899, i, 30, 125, 433, 494, 679, 700.)

G. T. M.

Hydrogenised Derivatives of Diphenylmethane and Triphenylmethane. By DANIEL VORLÄNDER (*Annalen*, 1899, 309, 348—355).—An introductory paper (see following abstracts).

M. O. F.

Formaldehyde Derivative of Dihydroresorcinol. By DANIEL VORLÄNDER and FRITZ KALKOW (*Annalen*, 1899, 309, 356—374. Compare Merling, Abstr., 1894, i, 177, and Vorländer and Kalkow, Abstr., 1897, i, 513).—The *sodium* derivative of methylenebisdihydroresorcinol crystallises in prisms and contains $2\text{H}_2\text{O}$. The anhydride (*octohydroxanthenedione*) forms the *oxime*, $\text{C}_{13}\text{H}_{17}\text{O}_3\text{N}_3$, which is microcrystalline, and melts at about 300°. Alcoholic ammonia converts methylenebisdihydroresorcinol into *decahydroacridinedione*, which has been described already. Nitrous acid transforms this substance into *octohydroacridinedione*,



which crystallises in white needles melting at 140—142°, and yields acridine when distilled with zinc dust; the *oxime* becomes brown above 200°, and melts and decomposes at 250°. A similar ketonic base, $\text{C}_{13}\text{H}_{13}\text{O}_2\text{N}$, obtained by distilling decahydroacridinedione, crystallises in flat needles and melts at 144°; the *hydrochloride* crystallises from water in colourless needles, and the *oxime* melts and decomposes at about 280°.

The ketonic acid, $\text{C}_{13}\text{H}_{18}\text{O}_5$, obtained from methylenebisdihydroresorcinol and caustic alkali, forms anhydrous *barium*, *silver*, and

lead salts; the *oxime* and *semicarbazone* melt at 159° and 218° respectively, and the *diethyl ester* boils at $235-240^{\circ}$ under 24 mm. pressure.

Methylenebismethylldihydroresorcinol, $C_{15}H_{20}O_4$, and *methylenebisdimethylldihydroresorcinol*, $C_{17}H_{24}O_4$, melt at 152° and $187-188^{\circ}$ respectively; the latter yields *tetramethyloctohydroxanthenedione*, $C_{17}H_{22}O_3$, which melts at 171° and, with alcoholic ammonia, forms *tetramethyldecahydroacridinedione*.

Methylenebisphenyldihydroresorcinol, $C_{25}H_{24}O_4$, melts at 212° ; *diphenyloctohydroxanthenedione*, $C_{25}H_{22}O_3$, melts at $225-226^{\circ}$.

Pentamethylctohydroxanthenedione, $C_{18}H_{24}O_3$, from dimethyldihydroresorcinol and acetaldehyde, melts at 174° . *Ethyltetramethyloctohydroxanthenedione*, $C_{16}H_{20}O_3$, melts at 139° . *Hexamethyloctohydroxanthenedione*, $C_{19}H_{26}O_3$, melts at 245° . M. O. F.

Compounds of Dihydroresorcinol with Aromatic Aldehydes. By DANIEL VORLÄNDER and O. STRAUSS (*Annalen*, 1899, 309, 375—383).—*Benzylidenebisdihydroresorcinol*, $C_{19}H_{20}O_4$, prepared from dihydroresorcinol and benzaldehyde, melts and decomposes at 208° , *phenyloctohydroxanthenedione*, $C_{19}H_{18}O_3$, melts at 255° , and the *p-nitro-derivative*, obtained from *p-nitrobenzaldehyde*, dihydroresorcinol, and glacial acetic acid, melts at 246° . *Phenyldecahydroacridinedione*, $C_{19}H_{19}O_2N$, produced on heating phenylhydroxanthenedione with alcoholic ammonia, does not melt below 310° , and forms, in alcohol, a colourless solution which exhibits blue fluorescence; distillation with zinc dust gives acridine.

Benzylidenebisdimethylldihydroresorcinol, $C_{23}H_{28}O_4$, obtained from dimethyldihydroresorcinol and benzaldehyde, melts at 193° ; *phenyltetramethyloctohydroxanthenedione*, $C_{23}H_{26}O_3$, melts at 200° . *Cuminyldienebisdimethylldihydroresorcinol*, $C_{26}H_{32}O_3$, melts at 173° .

Benzylidenebisphenyldihydroresorcinol, $C_{31}H_{25}O_4$, melts at 125° , water being eliminated; *triphenyloctohydroxanthenedione*, $C_{31}H_{26}O_3$, is identical with "benzylidenephenyldihydroresorcinol" (Vorländer and Erig, *Abstr.*, 1897, i, 275), and melts at 230° . *Triphenyldecahydroacridinedione*, $C_{31}H_{27}O_2N$, forms red solutions having green fluorescence. M. O. F.

Tautomerism of Isatin. By LEO MARCHLEWSKI (*J. pr. Chem.*, 1899, [ii], 60, 407—408. Compare *Abstr.*, 1896, i, 96 and 235).—When isatin reacts with *o*-phenylenediamine acetate in acid solution, a mixture of indophenazine and *o*-aminophenimesatine is formed; as the imesatine cannot be converted into the indophenazine under the conditions employed, it is clear that the isatin acts as a mixture of lactam and lactim.

Acids, such as acetic acid, appear to be able to cause the conversion of the lactim into lactam, as isatin when condensed with *o*-phenylenediamine in 50 per cent. acetic acid solution gives only a trace of imesatine, whilst the latter changes only excessively slowly into indophenazine when boiled with acetic acid of that strength. A. L.

Optically Active *trans*-Hexahydrophthalic Acids. By ALFRED WERNER and H. E. CONRAD (*Ber.*, 1899, 32, 3046—3055).—*trans*-Hexahydrophthalic acid is a racemic compound and is resolved

into its optically active components by fractional crystallisation of its quinine salts in alcoholic solutions; the neutral salt of the dextro-rotatory acid separates first, whilst the acid salt of the levorotatory acid remains dissolved. The anhydrides of the optically active acids, prepared by heating these compounds with acetic chloride, crystallise in broad plates, whilst the corresponding racemic compound separates in needles. The dimethyl esters were produced by heating the acids with methyl alcohol containing hydrogen chloride; the monomethyl esters were obtained by warming the anhydrides with methyl alcohol. The *monoamide* of the racemic acid was prepared by passing dry ammonia into an acetone solution of the inactive anhydride; it melts at 196°.

Active <i>trans</i> hexahydro-phthalic acids and derivatives.	$[\alpha]_D$.	M. p.	M. p. of racemic compound.
<i>d-trans</i> -Acid	18·2°	178—183°	215°
<i>l</i> - „ „	- 18·5		
<i>d</i> -Anhydride	- 76·7		
<i>l</i> - „ „	75·8	164°	140
<i>d</i> -Dimethyl ester ...	28·7		
<i>l</i> - „ „ ...	- 29·6	below 0°	33
<i>d</i> -Monomethyl ester.	26·5		
<i>l</i> - „ „ „	- 24·8	39°	96

cis-Hexahydrophthalic acid is not resolved into active components by the aid of quinine, cinchonine, or coniine; this acid differs from its *trans*-isomeride in forming the *acid potassium* salt, $C_8H_{11}O_4K + 3H_2O$.
G. T. M.

Constitution of Santonic and Metasantonic Acids and of Metasantonin. By LUIGI FRANCESCONI (*Gazzetta*, 1899, 29, ii, 181—257. Compare Abstr., 1898, i, 267).—A detailed account is given of the various transformations of santonic and metasantonic acids and of metasantonin.

Santonic acid dioxime, $C_{15}H_{22}O_4N_2$, is a white, friable substance which melts and decomposes at 120—125°; it dissolves readily in dilute halogen hydracids, alcohol, or ether. Its specific rotatory power is $[\alpha]_D - 102·4°$. It gives a *barium* salt, $(C_{15}H_{21}O_4N_2)_2Ba$.

With excess of phenylhydrazine, santonic acid gives the *phenylhydrazone* of *santonic acid phenylhydrazide*, $C_{27}H_{32}O_2N_4$, which is an orange-yellow powder melting and decomposing at 95°; it is readily soluble in alcohol, ether, or acetic acid.

Triketosantonic acid, $\begin{array}{c} CO \cdot CMe \cdot \overset{\overset{O}{\parallel}}{CH} \cdot CO \cdot \overset{\overset{O}{\parallel}}{C} \cdot OH \\ CO \cdot CMe \cdot \overset{\overset{O}{\parallel}}{CH} \cdot CO \cdot \overset{\overset{O}{\parallel}}{C} \cdot CHMe \cdot CO_2H \end{array}$ obtained by the action of bromine on santonic acid, forms glistening, straw-yellow needles melting and decomposing at 234°; it is readily soluble in ethyl acetate, alcohol, or water, the aqueous solution having an intense yellow colour. Its specific rotatory power in alcohol is $[\alpha]_D - 458·7°$. The *barium* salt, $C_{15}H_{12}O_7Ba + 2H_2O$, is a golden-yellow substance. The *ethyl* ester, $C_{14}H_{13}O_5 \cdot CO_2Et$, forms glistening, pale yellow needles which melt at 157—158° and dissolve readily in

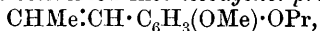
ethyl acetate or alcohol; the specific rotation in alcohol is $[\alpha]_D - 394.1^\circ$. The *dioxime*, $C_{15}H_{14}O_5(NO)_2$, is a hard, friable substance of a straw-yellow colour and is readily soluble in ether, alcohol, or water. The *anhydride* of the dioxime, $C_{15}H_4O_5 \begin{smallmatrix} \text{N} \\ \diagup \diagdown \\ \text{N} \end{smallmatrix} > O$, is a hard, friable, orange-coloured mass which softens at about 130° , melts and decomposes at 140° , and dissolves in the ordinary solvents.

Tribromo- α -santonin, $C_{15}H_{15}O_3Br_3$, obtained by the action of bromine on santonin acid, melts at $187-188^\circ$ and dissolves in ethyl acetate and to a less extent in ether, but is insoluble in solutions of alkali carbonates.

T. H. P.

Action of Sodium Methoxide on Dibromides of Propenyl Compounds and of Unsaturated Ketones. By F. J. POND, O. P. MAXWELL, and G. M. NORMAN (*J. Amer. Chem. Soc.*, 1899, 21, 955—967. Compare Pond and Beers, *Abstr.*, 1898, i, 645).—When isopropyl dibromide (Ciamician and Silber, *Abstr.*, 1890, 1294) is treated with sodium methoxide according to the method previously described, a ketone, $COEt \cdot C_6H(OMe)_2 \cdot O_2 \cdot CH_2$, is obtained which crystallises from alcohol in colourless prisms melting at 95.5° ; its *oxime* crystallises from methyl alcohol in colourless needles melting at 124° , and is readily reconverted into the ketone when heated with dilute sulphuric acid on the water-bath. The constitution of the ketone follows from the fact that it yields propionic acid when heated at 250° with concentrated sulphuric acid.

Eugenol propyl ether, $OPr \cdot C_6H_3(OMe) \cdot CH_2 \cdot CH : CH_2$, is a colourless oil boiling at 270.5° and having a sp. gr. 1.0032. Cahours (*this Journ.*, 1877, i, 461) gives its boiling point as $263-265^\circ$; when boiled with alcoholic potash, it is converted into *isoeugenol propyl ether*,



which distils at $280-281^\circ$ and forms large, colourless prisms melting at $53-54^\circ$; it may also be obtained by the action of propyl bromide on the potassium salt of isoeugenol. Its *dibromide* melts at $53-54^\circ$, is readily soluble in alcohol or ether, but cannot be recrystallised without decomposing; when treated with sodium methoxide, it yields the *ketone*, $COEt \cdot C_6H_3(OMe) \cdot OPr$, which, after distillation under reduced pressure, crystallises from methyl alcohol in large prisms melting at $63-64^\circ$, and boiling with slight decomposition at $284-287^\circ$ under atmospheric pressure. The *oxime*, $C_{13}H_{19}O_3N$, forms large crystals melting at 114° .

Benzylideneacetophenone (Claisen and Claparède, *Abstr.*, 1882, 512) yields a *dibromide* crystallising in small prisms and melting at 156° ; this dibromide is converted by the action of sodium methoxide into dibenzoylmethane (Baeyer and Perkin, *Abstr.*, 1884, 64; Claisen, *ibid.*, 1887, 575).

An unstable oil, probably the unsaturated ether $OMe \cdot CPh : CHBz$, has been isolated as an intermediate product; on treatment with dilute acids, it yields dibenzoylmethane.

Anisylideneacetophenone crystallises in fine, yellow needles melting at $77-78^\circ$; its *dibromide* crystallises in white prisms melting at $140-141^\circ$, and on treatment with sodium methoxide yields *anisoyl-*

benzoylmethane, $C_{16}H_{14}O_3$, crystallising in plates and melting at $131-132^\circ$. Bromine converts the diketone into a *bromine* derivative melting at $127-128^\circ$. J. J. S.

α -Oximinoketones and Quinoneoximes as Pseudo-acids. By R. C. FARMER and ARTHUR HANTZSCH (*Ber.*, 1899, 32, 3101—3109).—The criteria enumerated in this vol., i, 95, are applied to the cases in question. Isonitrosoacetone, $NOH:CH:CM_eO$, is neutral to litmus, is not appreciably dissociated, and does not form a compound with dry ammonia. But the sodium salt exhibits on dilution an increase of conductivity, $\Delta_{1024-32}$, only a little greater than in the case of salts of strong acids, and it is only slightly hydrolysed in aqueous solution. Consequently, isonitrosoacetone is a pseudo-acid, and its sodium salt has a different constitution, either $NO:CH:CM_eONa$, $CM_e \begin{smallmatrix} O \\ \diagup \diagdown \\ CH \end{smallmatrix} N \cdot ONa$, or $ONa \cdot CM_e \begin{smallmatrix} O \\ \diagup \diagdown \\ CH \end{smallmatrix} N$.

Quinonemonoxime, $NOH:C_6H_4:O$, does not unite with ammonia in benzene, and very slowly in ethereal, solutions; but its sodium salt exhibits the normal increase of conductivity on dilution, $\Delta_{1024-32}$; it must therefore be the salt of a comparatively strong acid, and hence quinoneoxime is a pseudo-acid. Quinoneoxime, in aqueous solution, has a decided acid reaction and a moderately large dissociation constant, and its very dilute solution has the same (greenish-yellow) colour as equivalent solutions of the red sodium (with $2\frac{1}{2}H_2O$) and green potassium salts (with $1H_2O$); hence the oxime itself undergoes a partial transformation in aqueous solution and the case is one of 'ionisation isomerism.' Quinonedioxime, on the other hand, has no appreciable conductivity, and its sodium salt is a true oxime salt, for it is largely hydrolysed in aqueous solution, as the abnormally large increase in conductivity on dilution, $\Delta_{1024-32}$, shows; indeed, the solution gradually deposits an *anhydride*, $(C_6H_4 \begin{smallmatrix} N \\ \diagup \diagdown \\ N \end{smallmatrix} O)_n$, a bright-red, amorphous, very stable substance. *o*-Toluquinoneoxime resembles its lower homologue, and "nitroso-orcinol" forms a very strongly acid solution. C. F. B.

Space Isomerism of the Ethers of Toluquinoneoxime. By W. CONGER MORGAN (*Amer. Chem. J.*, 1899, 22, 402—407).—The benzoyl derivative of toluquinone-*m*-oxime melting at 139° (Bridge and Morgan, *Abstr.*, 1899, i, 130) is completely converted into the stereoisomeride melting at 193° by heating with alcohol in a sealed tube for 3 hours at 120° ; the latter, under similar conditions, is not changed, but on raising the temperature to 150° , is completely decomposed. Caustic alkalis hydrolyse the compound of lower melting point to the corresponding oxime, which, however, on treatment with benzoyl chloride, yields the modification of higher melting point exclusively; the latter appears from these experiments to be the more stable form.

The phenomena described by Bridge and Morgan have been reproduced completely in the ethers formed by the interaction of acid chlorides with the sodium salt of the oxime prepared by the action of amyl nitrite on the sodium salt of *o*-cresol; since there is no

possibility of a nitro-compound being formed under these conditions, although this is not precluded in the action of nitrous acid on the cresols, the lower melting stereoisomerides cannot be considered as merely the higher melting compounds rendered impure by such admixture.

The *benzoate*, $C_{14}H_{10}O_3NBr$, of bromotoluquinone-*o*-oxime, prepared by boiling the corresponding dibromide, $C_{14}H_{11}O_3NBr_2$ (Bridge and Morgan, *loc. cit.*), with 75 per cent. alcohol, forms yellow crystals and melts at 184° . The *dichloride*, $C_{14}H_{11}O_3NCl_2$, of toluquinone-*o*-oxime benzoate crystallises from glacial acetic acid in short, thick, colourless prisms and melts at 149° ; when boiled with dilute alcohol, it loses hydrogen chloride and yields *chlorotoluquinone-*o*-oxime benzoate*, $C_{14}H_{10}O_3NCl$, which forms yellow crystals and melts and decomposes at $185\text{--}193^\circ$. All these compounds appear to exist in one form only.

W. A. D.

Isomerism in the Menthol Series. By IWAN L. KONDAKOFF and EUGEN LUTSCHININ (*J. pr. Chem.*, 1899, [ii], 60, 257—279).—Menthyl iodide, prepared by the action of hydriodic acid on either menthol or menthomenthene, boils at $124\text{--}126^\circ$ under a pressure of 18 mm., and has a sp. gr. 1.3836 at 0° and 1.3155 at 16.5° . It acts very rapidly on moist silver oxide, yielding tertiary menthomenthyl; the passage from secondary menthol to tertiary menthomenthyl is closely analogous to that from methylisopropylcarbinol to dimethylethylcarbinol.

Dihydrocarvone, prepared by oxidising the dihydrocarveol from *l*-carvone, boils at $221\text{--}224^\circ$, has a sp. gr. 0.9308 at 16° , a refractive index n_D 1.47243, the molecular refraction being 45.78; its specific rotation is $[\alpha]_D +17^\circ 27.5'$. The constants obtained for the product from *d*-carvone were as follows: boiling point, $221\text{--}222^\circ$; sp. gr. 0.9269 at 22° , refractive index $n_D = 1.46998$, molecular refraction 45.80, and specific rotatory power $[\alpha]_D -19^\circ 3.5'$. This dihydrocarvone is readily reduced by sodium and alcohol to pure dihydrocarvol boiling at $224\text{--}225^\circ$, and is readily converted into carvenone by Kondakoff and Gorbunoff's method (*Abstr.*, 1898, i, 145); the latter substance boils for the most part at $231\text{--}233^\circ$ under 763 mm., and at $101\text{--}103^\circ$ under 10 mm. pressure, but invariably leaves a residue which boils at $233\text{--}240^\circ$.

Klages' observation that carvenone may be obtained by treating dihydrocarvone with formic acid (*Abstr.*, 1899, i, 624) is the natural outcome of the work of Kondakoff and Gorbunoff; it is not necessary, however, to use anhydrous formic acid or to prolong the action; the product obtained by this method boils at 232° under 759 mm. pressure, and not at $232\text{--}235^\circ$ as stated by Klages.

Carvomenthol, obtained by reducing carvenone by Wallach's process (*Abstr.*, 1894, i, 44), boils at $220\text{--}221^\circ$ under 762 mm. pressure, but contains a fraction boiling at 240° ; it has a sp. gr. 0.9070 at 20.2° ; its refractive index is n_D 1.4672, its molecular refraction being 47.49. The foregoing carvomenthol was purified by conversion into tetrahydrocarvone as recommended by Wallach, but much loss is experienced in this process. The substance now boiled at 222° , had a

sp. gr. 0.9010 at 23°, a refractive index n_D 1.4696, and a molecular refraction 47.58.

Carvomenthol, prepared from specimens of active carone, varies considerably in optical activity, as do the derivatives prepared from it.

Carvomenthyl acetate, $C_{10}H_{19}OAc$, boils at 235—238° under 761 mm. pressure, and at 105—107° under 11 mm.; it is a colourless, fairly mobile liquid having a faint odour of cherries; it has a sp. gr. 0.9280 at 22°/4°, a refractive index n_D 1.45079, a molecular refraction 57.42, its specific rotation being $[\alpha]_D + 4.7'$.

Carvomenthyl chloride, $C_{10}H_{19}Cl$, is colourless and has an odour resembling menthyl chloride; it boils at 90—95° under 15 mm. pressure, and at 82—85° under 11 mm., is optically inactive, has a sp. gr. 0.9450 at 21°/4°, and refractive index n_D 1.46534 at 21°, the molecular refraction being 50.48. The *bromide*, $C_{10}H_{19}Br$, is colourless, boils at 95—99° under 10 mm. pressure, has a sp. gr. 1.1870 at 21°, a refractive index n_D 1.49060 at 21°/21°, and a molecular refraction 53.39.

Carvomenthene, prepared by heating carvomenthyl chloride or bromide with alcoholic potash, is divisible in two portions by fractional distillation, about 90 per cent. of the whole distilling at 172—174.5°, and the rest at 174.5—178°. It is a colourless, mobile liquid having an odour of menthene, is altered by exposure to air, and reacts readily with permanganate and with bromine.

The portion of the carvomenthene of lower boiling point has a sp. gr. 0.8230 at 16.5°/4°, a refractive index n_D 1.45979, molecular refraction 45.68, and a specific rotation $[\alpha]_D - 2.4'$. The fraction of higher boiling point had a sp. gr. of 1.8230 at 19°/4°, a refractive index n_D 1.46108, a molecular refraction 45.89, and a specific rotatory power $[\alpha]_D - 1.28$.

Carvomenthene hydrochloride boils at 90—98° under 18 mm., and at 89—95° under 16 mm. pressure; it has a sp. gr. 0.9390 at 19°/4°, a refractive index n_D 1.464941, the molecular refraction being 50.95, whilst its specific rotatory power is $[\alpha]_D - 1.22'$. Its properties are thus identical with those of carvomenthyl chloride, with the exception of the rotatory power.

Baeyer has shown (Abstr., 1893, i, 722) that carvomenthene combines with hydrogen bromide or iodide in the cold, yielding tertiary halogen derivatives, convertible through the intermediary of the corresponding acetates into a mixture of carvomenthene and tertiary carvomenthol. The authors have prepared the bromo-compound by heating the hydrocarbon with strong hydrobromic acid at 160—170°; it boils at 92—98° under 10 mm. pressure, has a sp. gr. 1.1620 at 20.5°/4°, a refractive index n_D 1.48822 at 20.5°, and a molecular refraction 54.27; it is optically inactive. Its properties are almost identical with those of carvomenthyl bromide, but it is highly probable that it consists of a mixture of the secondary and tertiary bromo-compounds, derived from two isomeric carvomenthenes in the parent hydrocarbon. The carvomenthene regenerated from the hydrobromide boiled at 172—175°, had a sp. gr. 0.8230 at 20°/4°, a refractive index n_D 1.45959, a molecular refraction 45.69, and a specific rotatory power $[\alpha]_D - 0.23'$.

Carvomenthyl chloride or bromide, on treatment with moist silver

oxide, affords tertiary carvomenthol and a small quantity of a substance, $C_{10}H_{22}O_3$, which crystallises in slender needles and melts at $101-102^\circ$.

It is not improbable that the behaviour of menthomenthol and carvomenthol illustrates a general law whereby hydro-aromatic alcohols containing the group $\cdot CHR \cdot CH(OH) \cdot$ are converted by halogen hydrides into tertiary halogen derivatives. The behaviour of fenchyl alcohol in this respect is being investigated. A. L.

Solubility of Camphor in Hydrochloric Acid. By AL. J. ZAHARIA (*Chem. Centr.*, 1899, ii, 308; from *Bul. soc. Sci. Bucuresti*, 1899, 8, 53—61).—Camphor is rather soluble in water and the aqueous solution becomes turbid on addition of sodium carbonate or sodium chloride solution. Camphor is very soluble in concentrated hydrochloric acid, and the more concentrated the acid and the lower the temperature the greater the quantity dissolved. On account of the volatility of camphor, the amount dissolved could not be determined. A saturated solution containing 35.74 per cent. of hydrochloric acid has a sp. gr. 1.1405. The acid solution of pure camphor is orange-yellow, and of impure camphor reddish-yellow, changing gradually to deep-red. Any excess of camphor is coloured light brown and may be dissolved with the exception of a small resinous residue by adding more hydrochloric acid. When a few drops of nitric acid are added to the hydrochloric acid solution, an oil separates which, when distilled or treated with water, again forms camphor. By electrolysing the hydrochloric acid solution, hydrogen is liberated at the cathode and a liquid is quickly formed at the anode, which by exposure to the air or treatment with water regenerates camphor. The amount of camphor in solution could not be determined polarimetrically, for the rotatory power depends on the quantity of hydrochloric acid present. When chlorine is passed into a hydrochloric acid solution of camphor, an oil is very slowly formed.

Camphor appears to behave towards hydriodic acid in a similar way. E. W. W.

Nitroso-derivatives of Caryophyllene and Cadinene and their bearing on the Characterisation and Classification of the Sesquiterpenes. By OSWALD SCHREINER and EDWARD KREMERS (*Pharm. Archives*, 1899, 2, 273—300. Compare Abstr., 1899, i, 619).—A pure specimen of caryophyllene, boiled at $136-137^\circ$ under 20 mm. pressure, had a sp. gr. 0.90301 at $20^\circ/20^\circ$, index of refraction n_D 1.49976 at 20° , and specific rotatory power $[\alpha]_D -8.959$ at 20° . The nitrosite is not polymerised, but has the simple formula $C_{15}H_{24}O_3N_2$, as shown by cryoscopic determinations in benzene solution; it has a specific rotatory power $[\alpha]_D$ of about +103 in 1.6 per cent. benzene solution, and, with benzylamine, it yields a product which melts at 167° . When exposed to sunlight in absolute alcoholic solution, it is transformed into a colourless (α) isomeride with the same molecular weight; this melts at $113-114^\circ$, is soluble in alcohol and benzene, and has no appreciable optical activity. When the nitrosite is exposed to sunlight in benzene solution, another colourless (β) substance is formed, which melts at $146-148^\circ$, and is insoluble in benzene or

alcohol; the yellow-orange rays are most active in effecting this change. The nitrosochloride can be obtained crystalline by mixing caryophyllene, alcohol, ethyl acetate, and ethyl nitrite, cooling in a freezing mixture, adding saturated alcoholic hydrogen chloride, leaving the whole in the cold for an hour, and then exposing it to sunlight; it melts and decomposes at 158° , and has the bimolecular formula $(C_{15}H_{24}ONCl)_2$; with benzylamine, it forms two derivatives, α and β , melting at 167° and 128° respectively; the former is the less soluble in alcohol. The nitrosate is also bimolecular; with benzylamine, it yields a product, melting at 128° , identical with the β -product obtained from the nitrosochloride. The hydrochloride of caryophyllene can be obtained crystalline by saturating an ethereal solution of the sesquiterpene with hydrogen chloride, and exposing the solution to intense cold; it melts at $69-70^{\circ}$.

When cadinene is mixed with glacial acetic acid, cooled with a freezing mixture, ethyl nitrate added, the mixture treated with strong nitric and glacial acetic acids, and diluted with alcohol, cadinene *nitrosate*, melting and decomposing at $105-110^{\circ}$, is precipitated. When a saturated solution of hydrogen chloride in glacial acetic acid is added, instead of the nitric and acetic acids, a *nitrosochloride*, melting and decomposing at $93-94^{\circ}$, is obtained.

C. F. B.

Oil and Terpenes from *Aralia nudicaulis*. By WILLIAM C. ALPERS (*Chem. Centr.*, 1899, ii, 623; from *Amer. J. Pharm.*, 71, 370-378).—The fresh root of *Aralia nudicaulis* contains 40-60 per cent. of water, and the dry drug yields on an average 5.53 per cent. of ash, which contains about 1.38 per cent. of sodium and potassium chlorides and sulphates. The dark red, fatty oil, obtained by extraction, has a sp. gr. 0.921 at 20° , is soluble in light petroleum, benzene, ether, or chloroform, slightly so in absolute alcohol, and insoluble in water; it solidifies at 3° , has acid number 7.3, saponification number 192, iodine number 106, and molecular weight of about 900; it consists chiefly of triolein. About 0.12 per cent. of an oil is obtained by distilling finely powdered aralia with steam; it has a pleasant, aromatic odour, and is composed mainly of a sesquiterpene, *araliene*, $C_{15}H_{14}$, which boils at 270° , has a sp. gr. 0.9086 at 20° , a specific rotatory power $[\alpha]_D -7$ to -8° , and a refractive index $n_D 1.49936$. It combines with hydrogen chloride to form an oily hydrochloride, but does not yield a solid bromide by the action of bromine. With a solution of hydrogen chloride in glacial acetic acid, it forms a bluish compound. The ethereal oil also contains a small quantity of a sesquiterpene alcohol, and a little azulene, $C_{16}H_{26}O$, which boils at about 300° .

E. W. W.

Liquorice Oil. By HEINRICH HAENSEL (*Chem. Centr.*, 1899, ii, 624; from *Pharm. Centr.-H.*, 40, 533).—By distilling Spanish liquorice root (*Glycyrrhiza glabra*), 0.03 per cent. of an ethereal oil is obtained; the Russian roots yield 0.035 per cent. These oils have a feeble acid reaction, which is possibly due to glycyrrhizic acid, but their composition is not identical, for whilst the Russian oil is dextrorotatory, the Spanish is levorotatory.

E. W. W.

Ethereal Oil of Poplar Buds. By FRITZ FICHTER and E. KATZ (*Ber.*, 1899, 32, 3183—3185).—The principal fraction obtained by distilling oil of poplar buds under diminished pressure is a terpene boiling at 132—137° under 13 mm. pressure, and at 263—269° under ordinary pressure; it has a sp. gr. 0.8926 at 15°/4°, and a specific rotatory power 10°48' at 22°; its vapour density corresponds with that of a sesquiterpene, $C_{15}H_{24}$.

The *nitrosochloride*, $C_{15}H_{24} \cdot NOCl$, obtained from the sesquiterpene and amyl or ethyl nitrite, and hydrochloric acid, separates as a crystalline powder from its solution in benzene or chloroform on the addition of methyl alcohol; it melts indefinitely, the range of temperature being 164—170°.

The *nitrolpiperidine* from the preceding compound and piperidine crystallises from alcohol and melts at 151—152°; the *nitrolbenzylamine* crystallises from alcohol in needles and melts at 132—133°; the *chlorides* of these substances have the composition $C_{15}H_{24}ON \cdot C_5NH_{10} + HCl$ and $C_{15}H_{24}ON \cdot NH \cdot CH_2Ph + HCl$ respectively.

The *nitroso-* or *isonitroso-sesquiterpene*, $C_{15}H_{22} \cdot NOH$, is obtained as an oil on treating the nitrosochloride with sodium ethoxide; on reduction, this substance yields an aminosesquiterpene.

The *nitrosite*, produced by the action of nitrous acid on the sesquiterpene, separates at first in blue needles melting at 127°; after crystallisation from alcohol, it becomes colourless and melts at 172°.

The *nitrosate* from the sesquiterpene, amyl nitrite, and nitric acid, crystallises from benzene and melts at 162—163°. The sesquiterpene does not yield crystalline additive compounds with bromine, hydrogen bromide, or hydrogen chloride, neither does it combine with elements of water (Wallach, *Abstr.*, 1893, 101). The properties of the sesquiterpene of poplar buds and its derivatives resemble those of the humulene in oil of hops (Chapman, *Trans.*, 1895, 67, 57 and 780). On the other hand, the sesquiterpene, although it may contain humulene, cannot consist wholly of this hydrocarbon, for the former is optically active whilst the latter is inactive.

The higher fractions of poplar oil contain a mixture of paraffins, "stearoptenes," consisting of the hydrocarbon $C_{24}H_{50}$ and its higher homologues; the total amount of paraffin in the oil is only $\frac{1}{2}$ per cent.
G. T. M.

Glucosides and Enzymes contained in the Root of some Spiræas. By MARTINUS W. BEYERINCK (*Chem. Centr.*, 1899, ii, 259; from *Centr. Bakt. Parasitenk.*, [ii], 5, 425—429).—The roots, rhizomes, and lower portions of *Spiræa ulmaria*, *S. filipendula*, and *S. palmata* contain a glucoside, gaultherin, and an enzyme, gaultherase, and by the interaction of these compounds methyl salicylate is formed. The elder portions of the roots and rhizomes of *S. kamschatica* also contain a second glucoside, spiræin, which is decomposed by gaultherase, forming salicylaldehyde. Gaultherin is prepared from the root nodules of *S. filipendula* by treating with boiling alcohol or boiling water, which dissolves the glucoside, but decomposes the enzyme. The glucoside could not be obtained in a crystalline form. Gaultherase, prepared from the same root by allowing the enzyme to

act on the glucoside and then extracting with alcohol, is soluble in water. It is not identical with emulsin, since it does not act on salicin or amygdalin, and gaultherin is not attacked by emulsin. By distilling the decomposition products formed in the production of gaultherase in steam, gaultheria oil is obtained. Hydrocyanic acid could not be detected in the products of the decomposition of gaultherin or of spiræin.

The presence of even 0.1 per cent. of gaultheria oil prevents the growth of mould. The odoriferous substances contained in plants may serve to protect them from insects. The merest traces of Capuchin oil are sufficient to prevent the growth of *Saccharomyces mycoderma*, but this oil has very much less effect on the lactic acid ferment or on acetic acid bacteria. This preventive action may be due to the presence of a hydroxybenzylthiocarbimide. E. W. W.

Derride and Pachyrhizide : Indian Fish Poisons. By H. E. TH. VAN SILLEVOLDT (*Chem. Centr.*, 1899, ii, 588—589 ; from *Ned. Tijds. Pharm.*, 11, 246—256 ; and *Arch. Pharm.*, 1899, 237, 595).—The stupefying fish poisons occur mainly in plants of the family of *Papilionaceæ*. Derride, $C_{33}H_{30}O_{10}$, prepared from the root of *Derris elliptica*, Benth., by treating with water, extracting with alcohol, evaporating, and treating the residue with ether, is a pale yellow substance, melts at 73° , and is easily soluble in the usual organic solvents, slightly so in light petroleum, and insoluble in water. The alcoholic solution has a faintly acid reaction. Derride is dissolved by sulphuric acid, forming a brownish-violet solution, from which it is reprecipitated by water, and it appears to combine with phenylhydrazine. By boiling with an alcoholic solution of hydrogen chloride, it forms an anhydro-derivative, $C_{33}H_{28}O_9$, which is also present in crude derride, and is not dissolved by ether. This compound forms small needles, melts at 214° , and when treated with hydriodic acid forms a compound, $C_{30}H_{19}O_6(OH)_3$, which melts at 240° .

The preparation of pachyrhizide, $C_{30}H_{24}O_{10}$, from the seeds of *Pachyrhizus angulatus*, Rich., is similar to that of derride. Pachyrhizide melts at 81° , and closely resembles derride. A compound, $C_{29}H_{20}O_9$, which is insoluble in ether and melts at 196° is also contained in the seeds. The anhydro-derivative of pachyrhizide, $C_{30}H_{22}O_9$, obtained by warming it with an alcoholic solution of hydrogen chloride, is a crystalline substance, melts at 182° , combines with phenylhydrazine, and contains two methoxy-groups.

Derride and pachyrhizide appear to belong to the same homologous series as Pfaff's timboin (*Abstr.*, 1891, 938), for which the formula $C_{34}H_{32}O_{10}$ may be calculated from his analyses. E. W. W.

Chlorophyll. By G. BODE (*J. pr. Chem.*, 1899, [ii], 60, 385—396).—A reply to Marchlewski (*Abstr.*, 1899, i, 381).

Phylloxanthin. By G. BODE (*Chem. Centr.*, 1899, ii, 529 ; from *Bot. Centr.*, 20, 227—239).—A continuation of the controversy with Marchlewski (*Abstr.*, 1899, i, 381). The alcoholic plant extract which contains chlorophyll combined with a lecithin is named crude

chlorophyll solution. By the action of weak acids, this compound undergoes an intramolecular change, being converted into the crystalline, olive-green chlorophyllan, and by the action of alkalis or of strong acids is decomposed into the lecithin constituents and alkali or acid compounds of chlorophyll; the latter (Marchlewski's alkachlorophyll and phyllocyanin) are decomposed by water. The chlorophyll compounds have different colours, according to the nature of the solvent and the concentration, which determine whether the compound remains undecomposed or is resolved into ions (compare Ostwald and J. Wagner; Deussen). Marchlewski's phylloxanthin is impure chlorophyllan and, like phyllotaonin, not really a chlorophyll derivative, whilst phylloporphyrin is a product formed from chlorophyll by an intramolecular change. E. W. W.

Furfuraldehyde from Beetroot and Molasses. By KARL ANDRLÍK (*Chem. Centr.*, 1899, ii, 460; from *Zeit. Zuck.-Ind. Böhm.*, 23, 551—559).—The colour of the furfuraldehyde-phloroglucide obtained from molasses is not the same as that of the pure compound. In an experiment in which large quantities were employed, about 7 per cent. of a substance which appeared to be methylfurfuraldehyde was found in the portion which distilled at 162—168°. E. W. W.

Constitution of Arginine. By ERNST SCHULZE and ERNST WINTERSTEIN (*Ber.*, 1899, 32, 3191—3194. Compare Abstr., 1898, i, 281; 1899, i, 107).—The formula previously proposed by the authors for arginine is confirmed by the fact that this substance is formed when ornithine is treated in the cold with cyanamide. Ornithine itself is probably α -diaminovaleric acid, since the distillation of its hydrochloride yields a small amount of a substance which gives the reactions of pyrrolidine, but has not yet been analysed. A. H.

Benzoyl Compounds of Hexon Bases. By D. LAWROFF (*Zeit. physiol. Chem.*, 1899, 28, 585—586).—A method is described of isolating the hexon bases by the use of benzoyl chloride and subsequent extraction with various solvents such as light petroleum. W. D. H.

An Alkaloid contained in the Bark of the Pomegranate. By ANTONIO PICCININI (*Gazzetta*, 1899, 29, ii, 311—318).—From the light petroleum mother liquors obtained in the preparation of methylgranatonine from the pomegranate root, an oily substance may be separated from which the author has isolated a *base* of the composition $C_9H_{17}ON$. On decomposing the picrate by means of potassium carbonate, it is obtained as a colourless oil which has a very faint basic odour and boils at 114—117° under 26 mm. pressure. It is soluble in water in all proportions, giving a strongly alkaline solution. The *picrate*, $C_{15}H_{20}O_8N_4$, forms a crystalline powder melting at 152—153° and soluble in boiling alcohol. The *aurichloride*, $C_9H_{17}ON \cdot HAuCl_4$, separates from dilute hydrochloric acid in orange-yellow rosettes and melts at 115—117°. The *hydrochloride* is a viscous mass soluble in water.

The base forms a *semicarbazone*, $C_{10}H_{20}ON_4$, which separates from

water in large, colourless, lustrous crystals which melt at 169° and dissolve in alcohol, but are insoluble in ether. The *hydrochloride*, $C_{10}H_{20}ON_4 \cdot HCl$, crystallises from dilute alcohol in slender, colourless needles which melt with decomposition and evolution of gas at 208° and are very soluble in water but insoluble in absolute alcohol; the aqueous solution of the hydrochloride gives a yellow, oily precipitate with a solution of gold chloride. T. H. P.

Abnormal Aurichlorides of Organic Bases. By GOTTFRIED FENNER and JULIUS TAFEL (*Ber.*, 1899, 32, 3220—3228. Compare *Abstr.*, 1898, i, 446).—The normal aurichloride of piperidine is always formed when auric chloride acts on piperidine hydrochloride in aqueous solution, and is also produced by the action of water on the abnormal salt. The latter is formed when piperidine hydrochloride and auric chloride are brought together in alcoholic solution, or when the normal salt is treated in alcoholic solution with hydrogen chloride or piperidine hydrochloride. It appears to dissociate when heated, either alone or in alcoholic solution, into the normal salt and piperidine hydrochloride. *Abnormal isopropylamine aurichloride*, $(C_3H_{10}N)_2AuCl_5$, is prepared in a similar manner to the piperidine compound, and is a golden-yellow, microcrystalline powder melting at 159° ; water decomposes it with formation of the normal salt. *Abnormal 1-methyl piperidine aurichloride*, $(C_6H_{14}N)_2AuCl_5$, melts between 80 and 88° and yields the normal salt when treated with water. In aqueous solution, 2:5-dimethylpyrrolidine yields an oily normal aurichloride, but in alcoholic solution an *abnormal aurichloride*, which crystallises in yellow plates melting at 102 — 104° . *Abnormal quinoline aurichloride* melts at 180° and decomposes at 260° .

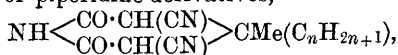
Methylamine, coniine, aniline, and pyridine do not appear to yield abnormal salts. A. H.

Synthesis of Glutaric and Trimethylene Derivatives. By ICILIO GUARESCHI and ERNESTO GRANDE (*Chem. Centr.*, 1899, ii, 439—440; from *Atti. Real. Accad. Torino*, 34. Compare *ibid.*, 33).—3:5-Dicyano-4-methyl-4-ethyltrimethylenedicarbonimide (*dicyanohomocaronimide*), $NH \begin{array}{c} \diagup CO \cdot C(CN) \\ | \\ CO \cdot C(CN) \end{array} \diagdown CMeEt$, prepared from the dibromide, $NH \begin{array}{c} \diagup CO \cdot CBr(CN) \\ | \\ C - CBr(CN) \end{array} \diagdown CMeEt$, by heating at 110° for a short time, crystallises in hard, lustrous, rhombic prisms, melts at 210° , and is slightly soluble in water. When heated with sodium hydroxide, the imide loses 1 mol. of ammonia, and the solution, after acidifying with acetic acid, forms a silver salt when treated with silver nitrate; by the action of hydrogen sulphide on this salt, an acid is obtained which is soluble in water and melts at 184° . Unlike dicyano-2:6-dioxy-4-methyl-4-ethylpiperidine, the dicarbonimide does not evolve ethane from neutral aqueous solutions, and even when heated to 240 — 245° gives only small quantities of carbon monoxide, methane, and ethane. The *ammonium* derivative of 3:5-dicyano-2:6-dioxy-4-dimethylpiperidine, prepared by the action of acetone on ethyl cyanoacetate in presence of alcoholic ammonia, forms a white, crystalline, easily soluble mass; its aqueous solution does not evolve gas even if

left for several days. The base, $\text{NH} \begin{smallmatrix} \text{CO} \cdot \text{CH}(\text{CN}) \\ \text{CO} \cdot \text{CH}(\text{CN}) \end{smallmatrix} \text{CMe}_2$, crystallises in lustrous, colourless leaflets, melts at $216-217^\circ$, and is slightly soluble in cold water, more so in alcohol or acetic acid. With potassium nitrite and sulphuric acid, it gives a characteristic, yellow coloration, and when heated at $310-320^\circ$ evolves methane. The *silver* derivative, $\text{C}_9\text{H}_8\text{O}_2\text{N}_3\text{Ag}$, forms a white, crystalline precipitate. The *dibromo*-derivative, $\text{C}_9\text{H}_7\text{O}_2\text{N}_3\text{Br}_2$, melts at $190-195^\circ$, and when heated for a long time with a 40 per cent. solution of acetic acid yields 3:5-dicyano-4-dimethyltrimethylenedicarbonimide, $\text{C}_9\text{H}_7\text{O}_2\text{N}_3$, which crystallises in small, hard, lustrous, colourless prisms, melts and decomposes at 242° , is soluble in water, alcohol, or acetic acid, and forms a silver salt. 3:5-Dicyano-2:6-dioxy-4-methyl-4-hexylpiperidine, prepared by the action of methyl hexyl ketone on ethyl cyanoacetate in presence of alcoholic ammonia, crystallises in broad, colourless leaflets, melts at $156-157^\circ$, is very slightly soluble in water, and decomposes in aqueous solutions, forming hexane and dicyanomethylglutaconimide, $\text{C}_8\text{H}_5\text{O}_2\text{N}_3$. The *dibromo*-derivative, $\text{C}_{14}\text{H}_{17}\text{O}_2\text{N}_3\text{Br}_2$, forms small, lustrous crystals, melts at 135° , loses its bromine when heated for several hours with a 50 per cent. solution of acetic acid, forming 3:5-dicyano-4-methyl-4-hexyltrimethylenedicarbonimide, $\text{C}_{14}\text{H}_{17}\text{O}_2\text{N}_3$; this compound crystallises in nacreous leaflets, melts at $154-155^\circ$, and is very slightly soluble in water.

Pinacolone does not react with ethyl cyanoacetate and ammonia.

The following conclusions are drawn: (1) By the action of ethyl cyanoacetate and ammonia on ketones of the type $\text{CH}_3 \cdot \text{CO} \cdot \text{C}_n\text{H}_{2n+1}$, the glutarimides or piperidine derivatives,



are formed. These compounds may also be regarded as derivatives of *aa*-dicyanoglutaric acids, $\text{C}_n\text{H}_{2n+1} \cdot \text{CMe}[\text{CH}(\text{CN}) \cdot \text{CO}_2\text{Et}]_2$. (2) These new saturated compounds form dibromo-derivatives from which trimethylene derivatives, $\text{NH} \begin{smallmatrix} \text{CO} \cdot \text{C}(\text{CN}) \\ \text{CO} \cdot \text{C}(\text{CN}) \end{smallmatrix} \text{CMe}(\text{C}_n\text{H}_{2n+1})$, may be prepared. Unlike the compounds of the preceding class, these substances, and the dibromo-derivatives from which they are prepared, do not give a yellow coloration with potassium nitrite and sulphuric acid.

E. W. W.

Action of Heat on Hydrogenised Compounds. By ICILIO GUARESCHI and ERNESTO GRANDE (*Chem. Centr.*, 1899, ii, 440; from *Atti Real. Accad. Torino*, 34. Compare this vol., i, 52).—(1) Cyano-trimethyldihydropyridone, $\text{C}_9\text{H}_{12}\text{ON}_2$, decomposes at $320-330^\circ$, forming mainly methane and cyanodimethylpyridone, which melts at $288-289^\circ$. (2) Cyanotetramethyldihydropyridone, $\text{C}_{10}\text{H}_{14}\text{ON}_2$, which melts at $142-143.5^\circ$, decomposes at $320-330^\circ$, forming methane and cyano-1-(?)-dimethylpyridone, $\text{C}_9\text{H}_{10}\text{ON}_2$; the latter melts at $203-204^\circ$. 3:5-Dicyano-2:6-dioxy-4-dimethylpiperidine, and other compounds which contain the group $\cdot\text{CH}_2 \cdot \text{CMeEt} \cdot$ or the group $\cdot\text{CH}_2 \cdot \text{CMe}_2 \cdot$, under similar conditions, yield methane or ethane. (3) Ethyl 2:4:6-trimethyldihydropyridinedicarboxylate, $\text{C}_{14}\text{H}_{21}\text{O}_4\text{N}$, decomposes at

340—350°, forming carbon dioxide, carbon monoxide, methane, ethylene, and alcohol, together with ethyl 2 : 6-dimethylpyridine-5-carboxylate, $C_{10}H_{13}O_2N$, and ethyl 2 : 6-dimethylpyridinedicarboxylate. Of these two esters, the former (compare Weiss, Abstr., 1886, 719) is a colourless base and boils at 255—257°, and the latter crystallises in long, colourless needles, melts at 73°, and boils at 300—305°. (4) Ethyl phenyldimethyldihydropyridinedicarboxylate, $C_{19}H_{23}O_4N$, prepared by the action of benzaldehyde on ethyl acetoacetate in presence of alcoholic ammonia, forms crystals and melts at 157°. On dry distillation, it decomposes into carbon dioxide, ethylene, hydrogen, and ethyl phenyldimethylpyridinecarboxylate, $C_{16}H_{17}O_2N$, which boils at 315—320°. Alcohol, benzene, carbon monoxide, and ethyl trimethylpyridinedicarboxylate are also formed by secondary reactions. (5) Ethyl dimethyldihydropyridinedicarboxylate, $C_{13}H_{19}O_4N$, prepared by the action of formaldehyde on ethyl acetoacetate in presence of alcoholic ammonia, crystallises in fluorescent needles, melts at 183°, and, on dry distillation under the ordinary pressure yields carbon monoxide, carbon dioxide, ethylene, ethane (?), ethyl dimethylpyridinecarboxylate, and ethyl dimethylpyridinedicarboxylate. The last compound melts at 73°, and is the principal product of the decomposition.

The results of these experiments show that the esters of dihydroacids decompose on distillation, liberating 1 mol. of hydrogen, which often takes part in secondary reducing actions, and that the carboxy-ethyl group of the original compound, or of the ester derived from it, also decomposes, forming carbon dioxide and ethylene.

E. W. W.

Pseudo-ammonium Bases. By ARTHUR HANTZSCH and M. KALB (*Ber.*, 1899, 32, 3109—3131. Compare Abstr., 1899, i, 400).—Pseudo-bases are neutral substances isomeric with true ammonium hydroxide bases, and correspond with the pseudo-acids previously described (Abstr., 1899, i, 399; this vol., i, 94, 103). Their existence may be discovered (1) by the phenomenon of gradual neutralisation, when the conductivity of a mixture of the ammonium chloride with sodium hydroxide gradually decreases to that of the sodium chloride produced, as the true base changes to the pseudo-base; (2) by 'abnormal neutralisation phenomena,' even where the velocity of change in (1) is too great to be observed, the neutral ammonium chloride giving a neutral solution with an equivalent of alkali, and the neutral pseudo-base giving a neutral salt when mixed with an equivalent of acid; (3) by the reluctance of the dry pseudo-base to combine with a dry acid or anhydride (CO_2 , HCN); (4) by the formation of abnormal anhydrides and ethers.

The ammonium cyanides resemble the hydroxides, and frequently pass into *pseudo*-salts which are insoluble in water, soluble in organic solvents, undissociated, and stable towards acids.

Methylpyridinium hydroxide, $C_5NH_5Me(OH)$, gave $\mu_{32} = 213$ and $\mu_{256} = 219$ at 25°; it is almost completely dissociated at moderate dilution and shows no tendency to pass into a pseudo-base.

1-Methylquinolinium 1-hydroxide, $C_9NH_7Me \cdot OH$, gave $\mu_{32} = 207.5$,

but is much less stable than the pyridine base, and passes into 1-methyl-1:2-dihydroquinoline oxide, $O(C_9NH_7Me)_2$, the anhydride of the pseudo-base; this separates in minute, white needles.

Methylisoquinolinium hydroxide gave $\mu_{32} = 206.9$, and, like the preceding base, rapidly undergoes change.

Phenylmethylacridinium hydroxide, $CPh \begin{smallmatrix} \swarrow C_6H_4 \\ \searrow C_6H_4 \end{smallmatrix} NMe \cdot OH$, gave $\mu_{256} = 117.5$ at 0° , falling to 57.4 in 10 minutes, 14.1 in 1 hour, and becoming zero in about 15 hours. For the chloride, $\mu_{128} = 45.6$ at 0° , and μ_∞ is calculated to be 50.0; whence μ_∞ for the base = 127.2, showing that it is as highly dissociated as the caustic alkalis. At 25° , the isomeric change proceeds very rapidly, especially during the first few seconds, and is complete within 6 hours. Phenylmethylacridol, $OH \cdot CPh \begin{smallmatrix} \swarrow C_6H_4 \\ \searrow C_6H_4 \end{smallmatrix} NMe$, the pseudo-base, is completely insoluble in water, to which it imparts not the slightest conductivity, and does not combine with carbon dioxide or hydrogen cyanide, although with strong acids it gives true acridinium salts; it is stable towards oxidising and reducing agents, and cannot therefore be represented by the formula $CHPh \begin{smallmatrix} \swarrow C_6H_4 \\ \searrow C_6H_4 \end{smallmatrix} NMe \cdot O$.

When liberated from the iodide by sodium hydroxide, dimethylacridinium hydroxide, $CMe \begin{smallmatrix} \swarrow C_6H_4 \\ \searrow C_6H_4 \end{smallmatrix} NMe \cdot OH$, is completely converted into the pseudo-base in 3 hours at 0° in *N*/512 solution and methylacridinium hydroxide within 20 minutes in *N*/256 solution. At 25° , 'gradual neutralisation' can no longer be observed, but 'abnormal neutralisation' occurs, the neutral iodides giving a neutral solution on adding an equivalent of caustic soda, whilst the pseudo-base is precipitated immediately, a separation which only takes place very slowly in the case of the phenylmethylacridinium base.

Phenylmethylacridine cyanide, $NMe \begin{smallmatrix} \swarrow C_6H_4 \\ \searrow C_6H_4 \end{smallmatrix} CPh \cdot CN$, separates gradually from a mixture of potassium cyanide and phenylmethylacridinium iodide as a white, crystalline substance, which melts at 176° , dissolves in organic solvents but not in water, and is not attacked by acids. The first product is the true cyanide,

$CPh \begin{smallmatrix} \swarrow C_6H_4 \\ \searrow C_6H_4 \end{smallmatrix} NMe \cdot CN$, which is stable at 0° , but is gradually converted into the 'pseudo-salt' at 25° , the conductivity reaching a minimum within 16 hours. The pseudo-base does not combine with hydrogen cyanide.

The azonium bases are regarded as pseudo-bases and show 'abnormal neutralisation' phenomena; thus the neutral salt $\begin{smallmatrix} N \\ | \end{smallmatrix} - C_6H_4 \begin{smallmatrix} \swarrow \\ \searrow \end{smallmatrix} NPhCl$ at once gives a neutral solution with an

equivalent of caustic soda and is converted into the pseudo-base $\text{N} \cdot \text{C}_6\text{H}_4 \cdot \text{NPh}$.
 $\text{CPh} \text{---} \text{CPh} \cdot \text{OH}$, which is quite insoluble in water, but dissolves in organic solvents.

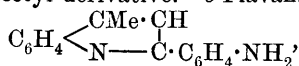
Aqueous solutions of cotarnine give evidence of the presence of a pseudo-base in the high temperature coefficient of the dissociation-constant and the formula $\text{C}_8\text{H}_6\text{O}_3 \langle \text{CH}(\text{OH}) \rangle \text{NMe}$ is suggested for *pseudocotarnine*. By the action of hydrogen cyanide on cotarnine, or of potassium cyanide on the hydrochloride, a cyanide is produced which is regarded as *pseudocotarnine cyanide*, $\text{C}_8\text{H}_6\text{O}_3 \langle \text{CH}(\text{CN}) \rangle \text{NMe}$; it melts at 86° , dissolves readily in organic solvents but only slightly in cold water, crystallises unchanged from water, and, unlike the true cyanides, is neutral, undissociated, indifferent to hydrochloric acid, and gives no precipitate with silver nitrate.

T. M. L.

Synthesis of 2- and 4-Hydroxyquinolines. By RUDOLF CAMPS (*Ber.*, 1899, 32, 3228—3234).—*o*-Acetaminoacetophenone is readily converted by aqueous soda into a mixture of 2-hydroxy-4-methylquinoline and 4-hydroxy-2-methylquinoline, the elements of water being eliminated.

A similar reaction is given by other acylaminoacetophenones, 2- or 4-hydroxy-derivatives, or a mixture of these, being formed, according to the constitution of the acid residues.

In addition to the two hydroxymethylquinolines, *o*-acetaminoacetophenone yields a small amount of *o*-aminoacetophenone and of *o*-flavaniline and its acetyl derivative. *o*-Flavaniline,



which has already been obtained in very small amount by Bischler (*Abstr.*, 1893, i, 531), crystallises in yellow needles melting at $83\text{--}84^\circ$; the *acetyl* derivative melts at 138° .

In the preparation of *o*-aminoacetophenone by the reduction of the corresponding nitro-compound, an oil boiling at $127\text{--}128^\circ$ under 16 mm. pressure is obtained, which yields indigo when heated in the air. Its constitution has not yet been ascertained.

A. H.

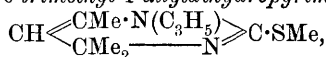
Carbamide and Thiocarbamide Derivatives of Diacetone-amine. By WILHELM TRAUBE and H. W. F. LORENZ (*Ber.*, 1899, 32, 3156—3163. Compare *Abstr.*, 1894, i, 170).—Anhydrodiacetone-phenylthiocarbamide may be represented by one or other of the following formulæ: $\text{CH} \langle \text{CMe} \text{---} \text{S} \rangle \text{C} \cdot \text{NHPh}$ or $\text{CH} \langle \text{CMe} \text{---} \text{N} \rangle \text{C} \cdot \text{SH}$; in accordance with the former, it should, as a derivative of penthi-azoline, have a basic character, whereas it reacts as a feeble acid forming metallic derivatives, the *silver* compound, $\text{C}_{13}\text{H}_{15}\text{N}_2\text{SAg}$, being described; the chemical behaviour of the substance is therefore more closely indicated by the second formula. The basic character of the pyrimidine ring is rendered manifest when the compound is alkylated, the methyl derivative being a strong base.

The *oxime*, $C_{13}H_9ON_3S$, of diacetonephenylthiocarbamide, obtained by treating this compound with alcoholic hydroxylamine, melts at $152-153^\circ$; the corresponding *phenylhydrazone*, $C_{19}H_{24}N_4S$, separates from alcohol in colourless crystals and melts at 169° .

2-Methothio-1-phenyl-4:4:6-trimethyldihydropyrimidine hydriodide, $C_{14}H_{18}N_2S, HI$, produced by mixing together alcoholic solutions of anhydrothiodiacetonephenylthiocarbamide and methyl iodide, separates from water in lustrous crystals.

Diacetoneallylthiocarbamide, $C_{10}H_{18}ON_2S$, crystallises from alcohol and melts at 138° ; its *phenylhydrazone* melts at 122° . The *anhydro*-compound is obtained either by heating the thiocarbamide above its melting point, or by treating it with warm dilute sulphuric acid; it crystallises from alcohol and melts at 130° ; its *silver* derivative is produced by treating the substance with an alcoholic solution of ammonia and silver nitrate.

2-Methothio-4:4:6-trimethyl-1-allyldihydropyrimidine,



obtained as an oily base by treating anhydrodiacetoneallylthiocarbamide with an alcoholic solution of methyl iodide and sodium methoxide, boils at 159° under a pressure of 580 mm.; its *platinichloride*, $(C_{11}H_{18}N_2S)_2 \cdot H_2PtCl_6$, forms orange-yellow crystals.

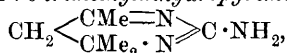
Anhydrodiacetonecarbamide (Abstr., *loc. cit.*) resembles the preceding anhydrothiocarbamides, and by analogy its formula should be $CH \begin{array}{c} \text{CMe} - NH \\ \text{CMe}_2 \cdot NH \end{array} > CO$.

Trinitroanhydrodiacetonecarbamide, $C_7H_9ON_2(NO_2)_3$, crystallises from methyl alcohol in colourless, silky needles which, when heated, take fire like gun cotton. The substance is a dibasic acid dissolving in alkalis and ammonia to form dark yellow solutions. The *barium* salt, $C_7H_7N_2(NO_2)_3Ba + 3H_2O$, crystallises in reddish-yellow needles; when heated, it explodes violently, and is decomposed by prolonged boiling with water. The *silver* salt, obtained in brown needles, is even more explosive.

The free acid, when boiled for some time with water, is converted into the compound $C_6H_9O_4N_3$; this substance, which is obtained by concentrating the solution under diminished pressure, crystallises in obliquely truncated prisms and melts at 214° ; it is a monobasic acid, and is not explosive; its *barium* salt, $(C_6H_8O_4N_3)_2Ba + 2H_2O$, is sparingly soluble in water.

G. T. M.

Action of Amidines on Mesityl Oxide and Phorone. By WILHELM TRAUBE and RUDOLF SCHWARZ (*Ber.*, 3163—3174. Compare Abstr., 1887, 932; 1894, i, 170; 1898, i, 121; and preceding abstract).—*2-Amino-4:4:6-trimethyldihydropyrimidine*,



prepared by heating a mixture of guanidine and mesityl oxide on the water-bath, crystallises from hot water in white, rhombic plates, melts at 145° , boils at 210° under a pressure of 10 mm., and sublimes in a vacuum, forming fern-like aggregates of slender needles. It

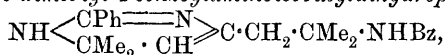
dissolves in water, alcohol, or benzene, and rapidly absorbs carbon dioxide from the air; it is a strong monoacidic base, its salts being decomposed by caustic alkalis but not by ammonia. The hydrochloride is very hygroscopic, the *oxalate* forms colourless crystals and melts at 238° , the *picrate* crystallises in needles and melts at 246° , and the *platinichloride*, $(C_7H_{13}N_2)_2 \cdot H_2PtCl_6$, and *mercurichloride* melt at $176-177^{\circ}$ and 184° respectively. The base takes up six atoms of bromine when treated with this reagent in glacial acetic acid solution; the product, when crystallised from warm water, forms reddish-purple, four-sided prisms which sinter together at 108° and melt at 113° ; when separating from boiling solutions, it appears as yellow needles, these sinter together at 108° but only melt at 137° ; the purple prisms appear to be an impure form (containing free bromine) of the yellow compound, $C_7H_{14}N_3Br_6$; the latter compound is decomposed on prolonged boiling with water. When aminotrimethyldihydropyrimidine is heated with acetic anhydride, it yields an oily *acetyl* derivative which has basic characters; its *platinichloride*, $(C_9H_{15}ON_3)_2 \cdot H_2PtCl_6$, crystallises in yellow leaflets and melts at $181-182^{\circ}$.

Diacetoneguanidine, $NH:C(NH_2) \cdot NH \cdot CMe_2 \cdot CH_2Ac$, prepared by heating a mixture of guanidine thiocyanate, mesityl oxide, and sodium ethoxide at 120° , crystallises from hot water in needles melting at 163° ; it was only obtained crystalline in one experiment, the product at other times being amorphous. The *acetyl* derivative, $C_9H_{17}O_2N_3$, produced by heating the crude base with acetic anhydride, crystallises from hot water in long needles and melts at 157° .

2-Phenyl-4 : 4 : 6-trimethyldihydropyrimidine (anhydrodiacetonebenzamidine), $CH_2 < \begin{smallmatrix} CMe_2 \cdot N \\ CMe_2 \cdot N \end{smallmatrix} > CPh$, obtained by heating benzamide and mesityl oxide on the water-bath, separates from methyl alcohol in colourless, acicular prisms and melts at 91° ; it is readily soluble in the ordinary organic solvents. The *hydrochloride*, $C_{13}H_{16}N_2 \cdot HCl + 2H_2O$, crystallises from alcohol in well-defined cubes and melts at 74° ; the *platinichloride*, $(C_{13}H_{16}N_2)_2 \cdot H_2PtCl_6 + 2H_2O$, crystallises in aggregates of rhombic plates and melts at 193° ; the *mercurichloride*, $C_{13}H_{16}N_2 \cdot H_2HgCl_3 + 2H_2O$, crystallises in flattened needles melting at 179° ; the *oxalate* crystallises in rosettes of leaflets and melts at $210-211^{\circ}$. *Anhydrotriacetonediguanidine*, $C_{11}H_{22}N_6$, results from the condensation of guanidine (2 mols.) with phorone (1 mol.), the reaction being assisted by heating on the water-bath; the product, a diacidic base, crystallises from water in long needles melting at $174-175^{\circ}$. The *hydrochloride*, $C_{11}H_{22}N_6 \cdot 2HCl$, crystallises in lustrous, rhombic plates and melts at 269° ; the *platinichloride*, $C_{11}H_{22}N_6 \cdot H_2PtCl_6 + H_2O$, crystallises in yellow leaflets and decomposes at 246° . *Triacetonedibenzamidine*, $CO(CH_2 \cdot CMe_2 \cdot NH \cdot CPh \cdot NH)_2$, obtained by heating together phorone and benzamidine and extracting the product with cold alcohol, crystallises from the alcoholic solution on the addition of light petroleum; it melts at 160° . The *nitrate* crystallises in prisms or six-sided plates; when separated slowly from warm water, it melts at 134° , but when repeatedly crystallised from rapidly cooled solutions, it melts at 218° . The *platinichloride*, $C_{23}H_{30}ON_4 \cdot H_2PtCl_6 + H_2O$

crystallises from hot water in four-sided leaflets and decomposes at 263—265°; the mercurichloride melts at 269°.

2-Phenyl-6 : 6-dimethyl-4-benzoylaminoisobutylldihydropyrimidine,

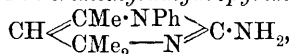


formed as a bye-product in the preceding condensation, is obtained in larger quantity when the reaction is carried out at 160—170°, or when the preceding base is heated to the same temperature; it crystallises from alcohol in four-sided, acicular prisms, and melts at 212°, sintering at 201°. The *hydrochloride*, $\text{C}_{23}\text{H}_{27}\text{N}_3\text{O} \cdot \text{HCl} + \text{H}_2\text{O}$, crystallises from hot water in six-sided prisms, sinters at 150°, and melts at 165°.

G. T. M.

Carbamide and Guanidine Derivatives of Diacetoneamine. By WILHELM TRAUBE and MAX SCHALL (*Ber.*, 1899, 32, 3174—3176. Compare preceding abstracts).—The cyclic anhydrodiacetonephenylthiocarbamide does not exchange its sulphur for oxygen, but the open chain diacetonephenylthiocarbamide, when boiled with yellow mercuric oxide and alcohol, yields an oil which is probably diacetonephenylcarbamide, for on further treatment with acetic acid 2-hydroxy-1-phenyl-4 : 4 : 6-trimethyldihydropyrimidine (anhydrodiacetonephenylcarbamide), $\text{CH} \begin{array}{c} \text{CMe} \cdot \text{NPh} \\ \text{CM}_{\text{e}_2} - \text{N} \end{array} \text{C} \cdot \text{OH}$, is produced; this substance crystallises from dilute alcohol in lustrous leaflets, melts at 161°, and dissolves in concentrated, but not in dilute, acids.

2-Amino-1-phenyl-4 : 4 : 6-trimethyldihydropyrimidine,



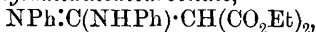
results when the removal of sulphur is effected by mercuric oxide in alcoholic ammonia; it melts at 161° and is a strong base, but its salts are ill-defined; the *platinichloride*, however, is crystalline.

Diacetoneolylthiocarbamide melts at 168°; when treated in succession with mercuric oxide and acetic acid, it yields 2-hydroxy-1-tolyl-4 : 4 : 6-trimethyldihydropyrimidine, which crystallises from dilute alcohol in needles melting at 151°.

Similar compounds are obtained with xylylcarbimide. G. T. M.

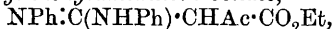
Additive Products of the Carbodiimides. By WILHELM TRAUBE and A. EYME (*Ber.*, 1899, 32, 3176—3178. Compare Abstr., 1898, i, 241, and 1899, i, 192).—The carbodiimides readily combine with ethyl malonate, ethyl acetoacetate, and similar substances in the presence of a trace of sodium ethoxide, yielding additive products having the general formula $\text{NR} : \text{C} : \text{NHR} \cdot \text{CHXY}$.

Ethyl diphenylethenylamidinedicarbonate,



produced from carbodiphenylimide and ethyl malonate, crystallises in colourless needles and melts at 167°. The corresponding *ditolyl* compound from carboditolylimide melts at 125°.

Ethyl acetyldiphenylethenylamidinedicarbonate,



from ethyl acetoacetate and carbodiphenylimide, melts at 109°; the *ditolyl* compound melts at 97°.

Diacetyldiphenylethenylamidine, $\text{NPh}\cdot\text{C}(\text{NHPh})\cdot\text{CHAc}_2$, from acetylacetone and carbodiphenylimide, melts at 150° ; the *ditolyl* compound melts at 149° . The combination does not take place unless sodium ethoxide is present; all the compounds produced are readily soluble in the ordinary organic solvents. G. T. M.

Preparation of Phenylindoxyl. By MARTIN HENZE (*Ber.*, 1899, 32, 3055—3060. Compare *Abstr.*, 1895, i, 371, and 1896, i, 696).—The following compounds were prepared in attempting to synthesise phenylindoxyl.

Phenyliminodiphenylacetic acid, $\text{NPh}(\text{CHPh}\cdot\text{CO}_2\text{H})_2$, produced either by melting together ethyl anilinophenylacetate and zinc chloride or by warming a mixture of anilinophenylacetic and bromophenylacetic acids at 100° , is a white, amorphous powder sintering at 90° and melting at $105\text{--}110^\circ$.

Tetraphenyl- $\beta\delta$ -diketopiperazine, $\text{CHPh}\langle\begin{smallmatrix} \text{NPh}\cdot\text{CO} \\ \text{CO}\cdot\text{NPh} \end{smallmatrix}\rangle\text{CHPh}$, obtained by heating a solution of anilinophenylacetic acid in acetic anhydride at 155° , is a white powder decomposing at 260° ; this reaction is reversed when the condensation product is boiled with sodium amyloxide.

Ethyl anthranilphenylacetate, prepared by boiling an alcoholic solution of anthranilic acid, ethyl bromophenylacetate, and sodium acetate, crystallises in white needles and melts at $175\text{--}176^\circ$, the *acid*, $\text{CO}_2\text{H}\cdot\text{C}_6\text{H}_4\cdot\text{NH}\cdot\text{CHPh}\cdot\text{CO}_2\text{H}$, melts at 227° . Neither this acid nor benzylanthranilic acid is affected by fusion with caustic alkalis at $209\text{--}300^\circ$. G. T. M.

Orthoquinonoid Structure of Saffranine, Oxazine, and Thiazine Colouring Matters. By ARTHUR G. GREEN (*Ber.*, 1899, 32, 3155—3156. Compare Kehrman, this vol., i, 62).—With reference to Kehrman's formulation of the azonium, oxazine, and thiazine colours as orthoquinonoid bases, it is pointed out that the author had previously expressed similar views (*Proc.*, 1892, 195, and 1896, 226), and had also given reasons for believing that oxygen and sulphur are quadrivalent in the latter compounds. The following are suggested as alternative formulæ, $\text{C}_6\text{H}_4\langle\begin{smallmatrix} \text{NCl} \\ \text{NR} \end{smallmatrix}\rangle\text{C}_6\text{H}_4$ and

$\text{C}_6\text{H}_4\langle\begin{smallmatrix} \text{NCl} \\ \text{O} \end{smallmatrix}\rangle\text{C}_6\text{H}_4$. These formulæ differ from those proposed by Kehrman, $\text{C}_6\text{H}_4\langle\begin{smallmatrix} \text{N} \\ \text{OCl} \end{smallmatrix}\rangle\text{C}_6\text{H}_4$, in containing the acidic radicle (chlorine in this case) attached to nitrogen and not to oxygen (or sulphur); this seems more probable in view of the more basic character of the nitrogen atom.

Another constitution for these substances is possible, namely, that in which both aromatic nuclei are represented as being quinonoid, $\text{C}_6\text{H}_4\langle\begin{smallmatrix} \text{NCl} \\ \text{NR} \end{smallmatrix}\rangle\text{C}_6\text{H}_4$ and $\text{C}_6\text{H}_4\langle\begin{smallmatrix} \text{NCl} \\ \text{O} \end{smallmatrix}\rangle\text{C}_6\text{H}_4$. In certain azonium compounds, it is found that both nuclei appear to be quinonoid, and react with amines; these formulæ offer a simple explanation of this behaviour, it being otherwise necessary to assume a migration of the

quinone linkings (Kehrmann, *Abstr.*, 1898, i, 439). Moreover, the formulæ suggested for the azonium bases render it possible to represent saffranones, rosindones, and similar anhydrides as *p*-anhydro-

compounds; $\text{O} \cdot \text{C}_6\text{H}_4 \cdot \text{N} \cdot \text{NR}$ or $\text{O} \cdot \text{C}_6\text{H}_4 \cdot \text{N} = \text{NR}$, this view of

their constitution being more probable than that based on Kehrmann's

formula, which represents them as *m*-anhydrides, $\text{O} \cdot \text{C}_6\text{H}_4 \cdot \text{N} \cdot \text{NR}$.
G. T. M.

Constitution of δ -Methyluric Acid. By ROBERT BEHREND and EMIL DIETRICH (*Annalen*, 1899, 309, 260—281).—Although uric acid contains only four replaceable atoms of hydrogen, five methyluric acids have been described (compare E. Fischer, *Ber.*, 1899, 32, 461). Of these compounds, δ -methyluric acid, which certainly contains the methyl radicle in the alloxan group, is regarded by Fischer as 4-methyl-

uric acid, $\text{NH} \cdot \text{CO} \cdot \text{C} \cdot \text{NH} \cdot \text{CO} \cdot \text{NMe} \cdot \text{C} \cdot \text{NH} \cdot \text{CO}$, along with α -methyluric acid (Hill) and ζ -methyluric acid (Fischer and Ach, this vol., i, 63). The authors' experiments, however, lead them to the conclusion that δ -methyluric

acid is 6-methyluric acid, $\text{NMe} \cdot \text{CO} \cdot \text{C} \cdot \text{NH} \cdot \text{CO} \cdot \text{NH} \cdot \text{C} \cdot \text{NH} \cdot \text{CO}$. If this is actually

the case, it would become necessary to reconsider the accepted formulæ of several purine derivatives. The results which have led to this conclusion are as follows. Besides acetylcarbamide and oxalic acid, methyluracil yields oxaluric and acetic acids when oxidised with potassium permanganate. In the same circumstances, β -dimethyluracil gives rise to acetylmethylcarbamide, and acetic, oxalic, and methyloxaluric acids; from α -dimethyluracil, methyloxaluric acid only is obtained, showing that the isomerides, so far as concerns the position of the methyl group, have the constitution $\text{NMe} \cdot \text{CO} \cdot \text{CH} \cdot \text{CO} \cdot \text{NH} \cdot \text{CMe}$.

Nitric acid converts α -dimethyluracil into nitromethyluracilcarboxylic acid, $\text{NMe} \cdot \text{CO} \cdot \text{C}(\text{NO}_2) \cdot \text{NH} \cdot \text{CO} \cdot \text{CO}_2\text{H}$, which loses carbon dioxide, yielding methylnitrouracil; the same methylnitrouracil is produced by methylating nitrouracil; it is the same substance from which von Loeben first prepared δ -methyluric acid.

β -Dimethyluracil, $\text{NMe} \cdot \text{CO} \cdot \text{CH} \cdot \text{CO} \cdot \text{NH} \cdot \text{CMe}$, occurring in the mother liquor of α -dimethyluracil (m. p. 219—220°), is produced when methyluracil, dissolved in alcoholic potash, is heated with methyl iodide, α -dimethyluracil and trimethyluracil being formed at the same time; it crystallises in serrated leaflets or long needles before precipitation, the purified substance forming lustrous prisms which melt at 260°.

Methyloxaluric acid, $\text{NH}_2 \cdot \text{CO} \cdot \text{NMe} \cdot \text{CO} \cdot \text{CO}_2\text{H}$, prepared by oxidising α -dimethyluracil, crystallises from water in prisms, and melts and decomposes at 180—190°, according to the rate at which the tempera-

ture rises ; the *potassium* salt forms a gelatinous mass which becomes crystalline.

Nitromethyluracilcarboxylic acid, obtained by the action of nitric and sulphuric acids on α -dimethyluracil, crystallises from water in needles or prisms containing the solvent, which is removed at 105° , the anhydrous substance melting at $255\text{--}256^\circ$; the *potassium* salt contains H_2O , and forms a *potassium nitrate* double salt.

Isodialuric acid is readily converted into dialuric acid under certain conditions, and if the analogous change took place when methylisodialuric acid is condensed with carbamide, 3-methyluric acid would be produced ; the authors find, however, that dialuric acid itself yields no trace of uric acid, but merely undergoes, in part, oxidation to alloxan.

M. O. F.

Deoxytheobromine. By JULIUS TAFEL (*Ber.*, 1899, 32, 3194—3206. Compare the following abstract).—When a solution of theobromine in 50 per cent. sulphuric acid is submitted to electrolytic reduction, *deoxytheobromine* (5-oxy-1:4-dimethyl-6:7-dihydro-*purine*), $\text{NH}\cdot\text{CH}_2\cdot\overset{\text{CO}\cdot\text{NMe}}{\underset{\text{CO}\cdot\text{NMe}}{\text{C}}}\cdot\overset{\text{N}}{\text{C}}\text{---}\text{N}\text{>CH}$, is formed ; it crystallises from water

in thin prisms containing $2\text{H}_2\text{O}$, which are sparingly soluble in cold, but very readily in boiling water ; the anhydrous base melts at 215° . The *hydrochloride* forms large, very soluble prisms, the *platinichloride* is a granular precipitate, the *picrate* decomposes at 205° , and the *mercurichloride* is a crystalline precipitate. Bromine in chloroform solution converts the base into an unstable *monobromo*-compound, $\text{C}_7\text{H}_9\text{O}_4\text{NBr}$, which readily passes into the isomeric 5-oxy-1:4-dimethylpurine hydrobromide. Deoxytheobromine is converted by oxidation with silver acetate, bromine, and acetic acid, or lead peroxide and acetic acid into 5-oxy-1:4-dimethylpurine, $\text{N}=\text{CH}\text{---}\overset{\text{CO}\cdot\text{NMe}}{\underset{\text{CO}\cdot\text{NMe}}{\text{C}}}\cdot\overset{\text{N}}{\text{C}}\text{---}\text{N}\text{>CH}$,

which crystallises, with $2\text{H}_2\text{O}$, in colourless prisms, and melts, when anhydrous, at $256\text{--}257^\circ$. This compound is also formed by the methylation of 5-oxy-1-methylpurine, its constitution and that of deoxytheobromine being thus determined. The *hydrochloride*, *hydrobromide*, *hydrogen sulphate*, *picrate*, and *platinichloride* are all crystalline salts.

A. H.

Deoxycaffeine. By THOMAS B. BAILLIE and JULIUS TAFEL (*Ber.*, 1899, 32, 3206—3220. Compare Abstr., 1899, i, 268, and the preceding abstract).—In addition to the salts of deoxycaffeine which have already been described, the *sulphate*, *nitrate*, *cuprochloride*, and *methiodide* have been prepared. When boiled with baryta water, the base yields carbon dioxide, formic acid, an amino-acid of unknown composition, ammonia (1 mol.), and methylamine (2 mols.). Bromine in absence of water converts deoxycaffeine into a monobromo-compound which is probably 5-oxy-1:4-dimethylpurine 6-methobromide, $\text{NMeBr}\cdot\text{CH}\cdot\overset{\text{CO}\cdot\text{NMe}}{\underset{\text{CO}\cdot\text{NMe}}{\text{C}}}\cdot\overset{\text{N}}{\text{C}}\text{---}\text{N}\text{>CH}$, whilst a yellow *perbromide* is formed when an excess of bromine is employed. Oxidation with lead peroxide and

acetic acid converts the base into *oxydimethylpurine methoacetate*,

$$\begin{array}{c} \text{NMeAc} \cdot \text{CH} \cdot \text{C} \cdot \text{NMe} \\ | \quad | \\ \text{CO}-\text{NMe}-\text{C}-\text{N} \end{array} \gg \text{CH}$$
, which is converted by alkalis into 5-*oxy-*

1:4-*dimethylpurine 6-methohydroxide*,

$$\begin{array}{c} \text{OH} \cdot \text{NMe} \cdot \text{CH} \cdot \text{C} \cdot \text{NMe} \\ | \quad | \\ \text{CO}-\text{NMe}-\text{C}-\text{N} \end{array} \gg \text{CH}$$
;

this decomposes and melts at 160°, is stable in the air, and does not absorb carbon dioxide, whilst the solution is strongly alkaline and behaves in every way like that of a strong ammonium base. It is therefore probable that the constitution of the dry salt is represented

by the formula

$$\begin{array}{c} \text{NMe} \cdot \text{CH} \cdot (\text{OH}) \cdot \text{C} \cdot \text{NMe} \\ | \quad | \\ \text{CO}-\text{NMe}-\text{C}-\text{N} \end{array} \gg \text{CH}$$
, and that of the base in

solution by the alternative formula just given. The *chloride*, *bromide*, *picrate*, *platinichloride*, and *aurichloride* have all been prepared. The same base is formed when 5-*oxy-1:4-dimethylpurine methiodide* is converted into the acetate, and the latter decomposed by alkali. From this it follows that the methohydroxide has the constitution assigned to it above, whilst deoxycaffeine is 5-*oxy-1:4:6-trimethyl-*

6:7-*dihydropurine*,

$$\begin{array}{c} \text{NHMe} \cdot \text{CH}_2 \cdot \text{C} \cdot \text{NMe} \\ | \quad | \\ \text{CO}-\text{NMe}-\text{C}-\text{N} \end{array} \gg \text{CH}$$
. When the methohydroxide is heated at 170–180°, caffeine and deoxycaffeine are formed along with decomposition products of the latter. A. H.

Constitution of the so-called Oxyazo-compounds. By R. C. FARMER and ARTHUR HANTZSCH (*Ber.*, 1899, 32, 3089–3101).—The criteria enumerated in this vol., i, 95, are applied to the case in question. Free quinonehydrazone (“hydroxyazobenzene”) is neutral to indicators, is not an electrolyte, and does not form a compound with ammonia in benzene solution; its constitution is probably $\text{NHPh} \cdot \text{N} \cdot \text{C}_6\text{H}_4 \cdot \text{O}$ (and that of its hydrochloride, $\text{NH}_2\text{PhCl} \cdot \text{N} \cdot \text{C}_6\text{H}_4 \cdot \text{O}$). But it is a pseudo-acid, for its *sodium* salt, with $3\text{H}_2\text{O}$, is only hydrolysed to the extent of about 0.3 per cent. at dilution V_{32} , and therefore must be derived from a comparatively strong acid, probably having the formula $\text{NPh} \cdot \text{N} \cdot \text{C}_6\text{H}_4 \cdot \text{ONa}$; moreover, the quinonehydrazone dissolves in aqueous ammonia, probably having undergone a molecular transformation into the hydroxyazo-compound, which then united with ammonia. *p*-Quinonephenylhydrazone forms alkali salts most easily; the *o*-quinonephenylhydrazones (from *o*-toluquinone and from pseudocumquinone) do so less readily and the products are less stable; the meta-isomeride could not be obtained. β -Naphthalene-*o*-quinonephenylhydrazone will only form a salt when treated with the alkoxide; the *p*-chloro- and *p*-nitro-phenylhydrazones form salts with concentrated aqueous potash, but the salts are decomposed by water.

The abnormal hydrates, $\text{NHPh} \cdot \text{N} \cdot \text{C}_6\text{H}_4(\text{OH})_2$ (Hewitt, *Abstr.*, 1895, 353), occupy a position intermediate between the quinonehydrazones and hydroxyazo-compounds; they are best prepared by treating the hydrochlorides of the quinonehydrazones with water or aqueous sodium carbonate or acetate, and they contain 1, or more often $\frac{1}{2}$, H_2O ; a number were prepared, although not all for the first time. Some benzoates and acetates were prepared from the quinone-

hydrazones or their hydrates, and methyl derivatives (azoanisoles, $\text{NR:N}\cdot\text{C}_6\text{H}_4\cdot\text{OMe}$) were prepared from the sodium or silver salts, and also from the nitrosohydrocarbon and the anisidine; in no case was a nitrogen-ether obtained. No hydrazone could be obtained from quinone and phenylhydrazine; quinol, and an oxidation product of phenylhydrazine, diphenyltetrazone, being obtained instead.

The following compounds are, perhaps, new. Derivatives of (*p*-) quinone: *m*-chlorophenylhydrazone, the *methyl* derivative is yellow and melts at 53° ; *o*-tolylhydrazone, the *acetate* melts at 65° , and the *methyl* derivative is brown and melts at 59° ; pseudocumenehydrazone, the *hydrochloride* melts at 162° , and the *methyl* derivative is brown and melts at 89° . Derivatives of *o*-chloroquinone: the *phenylhydrazone* is yellow and melts at 88° , the *hydrochloride* melts at 150° , the *hydrate*, which is brick-red below 50° and yellow above, melts at 73° ; *o*-tolylhydrazone, the *hydrochloride* melts at 148° . Derivatives of *o*-toluquinone: *m*-chlorophenylhydrazone is yellow and melts at 104° , the *hydrate* is red, melts at 76° , does not lose water readily, and is not dissociated in benzene solution, as cryoscopic experiments show, the *benzoate* is pale yellow and melts at 101° ; *o*-tolylhydrazone, the *hydrochloride* melts at 157° , another *hydrate* is brick-red, effloresces readily, and melts at 83° .
C. F. B.

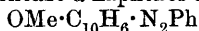
Constitution of the Hydroxyazo-compounds. By WILLIAM MCPHERSON (*Amer. Chem. J.*, 1899, 22, 364—383).—The early portion of this paper contains details of work already published in brief (*Abstr.*, 1896, i, 27); that the *p*-hydroxyazo-compounds have the constitution denoted by their names, and are not quinone derivatives of the type $\text{O:R:N}\cdot\text{NPh}$, is held to be established by the following facts. (1) *p*-Hydroxyazobenzene by direct acylation or alkylation, yields derivatives unquestionably of the type $\text{NPh:N}\cdot\text{C}_6\text{H}_4\cdot\text{OR}$ ($\text{R}=\text{acyl}$ or alkyl), although *o*-hydroxyazo-compounds give by acylation derivatives as unquestionably of the form $\text{O:R:N}\cdot\text{NPhAc}$ (Goldschmidt and others). (2) The free *p*-hydroxyazo-compounds do not interact with phenylhydrazine at 100° , although all *p*-quinone-benzoylphenylhydrazones react explosively with this substance. (3) All *p*-hydroxyazo-compounds are readily soluble in dilute caustic alkalis, whilst the *o*-hydroxyazo-compounds derived from naphthalene, which are undoubtedly quinonephenylhydrazones, are insoluble. (4) The results obtained in the cryoscopic researches of Auwers and Orton (*Abstr.*, 1897, i, 40, and ii, 112).

The hydrazones described were prepared by the interaction of the quinones with salts of the respective hydrazines.

Quinoneacetylphenylhydrazone, $\text{O:C}_6\text{H}_4\cdot\text{N}\cdot\text{NPhAc}$, crystallises from a mixture of benzene and light petroleum in flat, yellow needles, melts at 118° , and is not identical with *p*-acetoxyazobenzene, $\text{NPh:N}\cdot\text{C}_6\text{H}_4\cdot\text{OAc}$ (Wallach and Kiepenheuer, *Ber.*, 1881, 14, 2617), which melts at 89.5° , not $84\text{--}85^\circ$; when heated with alcoholic potash, however, it yields *p*-hydroxyazobenzene. *Toluquinonebenzoylphenylhydrazone*, $\text{O:C}_6\text{H}_3\text{Me:N}\cdot\text{NPh}\cdot\text{COPh}$, crystallises from benzene in small, square, yellow plates, and melts at 151° ; when reduced with zinc dust and acetic acid, it yields benzanilide, and is converted by

alcoholic potash into benzeneazo-*o*-cresol, although not identical with the benzoate of the latter (Noelting and Kohn, Abstr., 1884, 901; compare Goldschmidt and Pollak, Abstr., 1892, 974). *Thymoquinonebenzoylphenylhydrazine*, $\text{O}:\text{C}_6\text{H}_2\text{MePr}^\beta:\text{N}:\text{NPh}\cdot\text{COPh}$, crystallises from a mixture of benzene and light petroleum in yellow plates and melts at 132° ; there is also formed a colourless, crystalline substance, $\text{C}_{15}\text{H}_{14}\text{O}_2\text{N}_2$, melting at 155° . The hydrazone, on reduction with zinc dust and acetic acid, yields benzeneazothymol, but is not identical with the benzoate of the latter, $\text{OBz}\cdot\text{C}_6\text{H}_2\text{MePr}^\beta\cdot\text{N}_2\text{Ph}$, prepared by Baumann's reaction, which crystallises from hot alcohol in reddish-yellow needles, melts at 115° , and is converted by alcoholic potash into the parent substance. *α -Naphthaquinonebenzoylphenylhydrazine* crystallises from a mixture of benzene and light petroleum in yellow, silky needles, and melts at 161.5° ; it is not identical with benzeneazo- α -naphthyl benzoate (Meldola, Trans., 1889, 55, 606).

When benzoquinone and α -phenylmethylhydrazine hydrochloride are brought together in aqueous solution, nitrogen is evolved and diphenyldimethyltetrazone formed; with toluquinone and thymoquinone, similar action occurs. *Diphenyldibenzyltetrazone*, $\text{N}_2(\text{NPh}\cdot\text{C}_7\text{H}_7)_2$, obtained similarly from benzoquinone and α -phenylbenzylhydrazine sulphate, crystallises from a mixture of benzene and light petroleum in colourless rhombohedra, and melts and decomposes at 145° . *α -Naphthaquinonephenylmethylhydrazine*, $\text{O}:\text{C}_{10}\text{H}_6:\text{N}\cdot\text{NMePh}$, crystallises in long, flat, amethyst-coloured crystals, melts at 118.5° , and is not identical with 4-benzeneazo- α -naphthol-1-methyl ether,



(Zincke and Bindewald, Ber., 1884, 17, 3026). *α -Naphthaquinonephenylbenzylhydrazine*, $\text{O}:\text{C}_{10}\text{H}_6:\text{N}\cdot\text{NPh}\cdot\text{C}_7\text{H}_7$, crystallises from a mixture of benzene and light petroleum in yellow, dichroic, flat needles and melts at 136° ; the benzyl ether, $\text{C}_7\text{H}_7\cdot\text{O}\cdot\text{C}_{10}\text{H}_6\cdot\text{N}_2\text{Ph}$, prepared by the action of benzyl chloride and caustic soda on benzeneazo- α -naphthol, forms ruby-red monoclinic crystals, and melts at 102° .

The benzoyl derivative, $\text{O}:\text{C}_{10}\text{H}_6:\text{N}\cdot\text{NPhBz}$, is obtained by the action of benzoyl chloride on an alcoholic solution of β -naphthaquinonephenylhydrazine and sodium ethoxide, and also by the interaction of β -naphthaquinone and α -benzoylphenylhydrazine sulphate; it forms yellow needles, melts at 191° , and on hydrolysis with alcoholic potash or concentrated sulphuric acid, yields benzoic acid and β -naphthaquinonephenylhydrazine. When the latter is heated with methyl iodide and alcoholic sodium methoxide, the methyl ether of 2-benzeneazo- α -naphthol is formed (compare Meldola and Hanes, Trans., 1894, 65, 834; Noelting and Grandmougin, Abstr., 1891, 1076), which crystallises from alcohol in reddish-yellow plates and melts at 95° ; *β -naphthaquinonephenylmethylhydrazine* crystallises from alcohol in yellow needles and melts at 134.5° .

W. A. D.

Action of Benzoyl Chloride on the Phenylhydrazones of Benzoin. By PAUL C. FREER (*Amer. Chem. J.*, 1899, 22, 396—402. Compare Smith, Abstr., 1899, i, 909).—The product of the action of benzoyl chloride on benzoin- β -phenylhydrazine dissolved in absolute ether at "winter temperature," consists principally of

benzanilide and benzil, together with lophine, dibenzoylaniline, hydrogen chloride, ammonium chloride, and aniline hydrochloride, but a considerable amount of resin is also formed; *m*-nitrobenzoyl chloride, under similar conditions, gives rise to *m*-nitrobenzoylaniline, but the action of benzoyl chloride on benzoin- β -phenylhydrazone methyl ether yields only an intractable resin. The author discusses the nature of these reactions at some length, on the assumption that the compound, $\text{NH} \begin{smallmatrix} \text{CPh} \\ \text{NPh} \end{smallmatrix} \text{CPh}$, is initially formed; the formation of lophine from benzoin- β -phenylhydrazone is explained by assuming that the latter first dissociates into benzaldehyde and the group $\text{:CPh}\cdot\text{NH}\cdot\text{NHPh}$, the benzaldehyde subsequently combining with the benzil and ammonia simultaneously formed.

The author reiterates his statement (Abstr., 1899, i, 357) that benzoin- α -phenylhydrazone is not affected by benzoyl chloride.

W. A. D.

Unsymmetrical Disubstituted Hydrazones. By HANS LABHARDT and K. VON ZEMBRZUSKI (*Ber.*, 1899, 32, 3060—3063).—The phenylhydrazones of benzaldehyde, salicylaldehyde, and their homologues are white or pale yellow; the hydrazones containing nitro-groups and their sulphonic acids are either yellow or red, the latter compounds dyeing wool and silk from acid baths. The hydrazones derived from secondary hydrazines and aromatic aldehydes have similar properties and the following compounds of this type are described:

Phenyl-p-nitrobenzylidenemethylhydrazine, $\text{NMePh}\cdot\text{N}:\text{CH}\cdot\text{C}_6\text{H}_4\cdot\text{NO}_2$, obtained by mixing equivalent amounts of *p*-nitrobenzaldehyde and α -phenylmethylhydrazine in alcoholic solution, melts at 132° ; the *m*-nitro-compound melts at 112° and the *o*-nitro- at 77° ; these substances form red crystals readily soluble in the ordinary organic solvents; the para-compound may also be produced by methylating phenyl-*p*-nitrobenzylidenemethylhydrazine.

Phenyl-o-hydroxybenzylidenemethylhydrazine crystallises in white needles and melts at 71° ; its solution in alcoholic potash is yellow.

Phenyl-p-nitrobenzylidenemethylhydrazine melts at 131° and the *m*-nitro-compound at 114° ; these substances are red, whilst the *o*-nitro-derivative, which melts at 44° , crystallises in brownish-yellow needles.

Diphenyl-p-nitrobenzylidenemethylhydrazine melts at 131° , the *m*-nitro-compound at 119 — 120° ; both these substances are brownish-yellow; the *o*-nitro-compound melts at 146° and is yellowish-red; the *o*-hydroxy-compound crystallises in white needles and melts at 139° .

p-Tolyl- α -methylhydrazine, prepared by reducing *p*-tolylmethylnitrosamine, is a non-crystallisable oil, readily soluble in the ordinary organic solvents; it is decomposed by concentrated mineral acids, its hydrochloride being most conveniently obtained by passing hydrogen chloride into its ethereal solution.

p-Tolyl-p-nitrobenzylidenemethylhydrazine melts at 143° , the *m*-nitro-compound at $150\cdot5^\circ$, and the *o*-nitro-compound at $90\cdot5^\circ$; these nitro-derivatives are red, whilst the *p*-hydroxy-compound melting at 85 — 86° , is pale yellow.

G. T. M.

Normal Diazo-compounds as "Pseudodiazonium Compounds." By ARTHUR HANTZSCH (*Ber.*, 1899, 32, 3132—3136).—The relation of normal diazo-compounds (metallic salts, diazo-oxides, diazo-ethers, and normal diazo-cyanides) to diazonium salts exactly corresponds with that of the pseudo-bases (see this vol., i, 113) to the ammonium salts. The non-existence of the isomeric diazonium compounds corresponds with the labile or unstable nature of the ammonium bases, their cyanides and other derivatives, the velocity of change being here too great to be observed.

The latter part of the paper is a reply to Bamberger (*Abstr.*, 1899, i, 750). T. M. L.

Decomposition of Proteids by Acids. By THOMAS BOKORNY (*Zeit. angew. Chem.*, 1899, 1099—1100).—The action of 4 per cent. aqueous solutions of hydrochloric, hydrobromic, sulphuric, oxalic, and acetic acids on purified egg-albumin has been studied. The action begins soonest with hydrochloric acid, and the others follow in the order given. The albumoses and peptones formed were separately precipitated after the several mixtures had been boiled for 2 hours. Moderately large quantities of peptone were obtained from the hydrochloric, hydrobromic and sulphuric acid solutions, none at all from the oxalic acid, and merely a trace from the acetic acid. Compare Wroblewski on peptonisation (*Abstr.*, 1895, ii, 516).

J. J. S.

Amount of Tyrosine from Proteids. By FELIX REACH (*Virchow's Archiv*, 1899, 158, 288—296).—The amount of tyrosine obtained from the decomposition of various proteids is very differently given by different observers, and also differs considerably with different proteids (from 0.25 to 5 per cent.).

In the present research, the proteid material was decomposed by pancreatic digestion, but in parallel experiments with the same proteid the results vary. Thus with fibrin, the amount of tyrosine varied from 0.6 to 3.8; with egg-white from 0.1 to 0.6; with muscle proteids, from 1.06 to 1.37 per cent. The one experiment quoted with casein gave a yield of 4.5 per cent. of tyrosine. W. D. H.

Nomenclature of the Albumins of White of Egg. By ALEXEI A. PANORMOFF (*Chem. Centr.*, 1899, ii, 480; from *J. Russ. Chem. Soc.*, 1899, 31, 555—556).—The eggs of different birds contain different kinds of albumin, and the author proposes to name the albumin of hen's egg, which is easily crystallised from ammonium sulphate solution, albumin, and the more soluble albumin, albuminin (compare *Abstr.*, 1899, i, 655). In other cases, to the albumin which is least soluble in ammonium sulphate solution a name is given which is formed by attaching the termination "in" to the zoological name of the bird, the more soluble albumins being similarly designated by words ending in "inin" and "inidin" in the order of increasing solubility. Thus the amorphous albumin of pigeon's egg is columbin and the more soluble crystalline albumin is columbinin. E. W. W.

Action of Heat, Dilute Acids, and Alcohol on Albumin. By ALEXEI A. PANORMOFF (*Chem. Centr.*, 1899, ii, 480—481; from *J. Russ. Chem. Soc.*, 1899, 31, 556—560. Compare Abstr., 1899, i, 655).—When 0.05—0.5 per cent. solutions of albumin in hydrochloric, hydrobromic, phosphoric, pyrophosphoric or metaphosphoric acid are dialysed at the ordinary temperature, acid solutions are obtained in all cases but the last, metaphosphoric acid alone forming a precipitate. The rotatory power of these acid solutions differs from those of the original solutions and is still further increased by heating at 100°. In both cases, compounds of albumin with the acids are formed, and the change of rotatory power must therefore be due to polymerisation or depolymerisation. These polymeric compounds have also a different solubility in water. The compounds obtained by dialysing the cold solutions, when reduced, regenerate the original albumin, but the compounds prepared by heating at 100° yield only amorphous compounds of the same composition. The formula $\text{Alb}, 5\text{HCl}$, in which $\text{Alb} = \text{C}_{258}\text{H}_{422}\text{O}_{63}\text{N}_{63}\text{S}_3$, is ascribed to the hydrochloride and $\text{Alb}, 3\text{HBr}$ to the hydrobromide. Phosphoric acid forms compounds containing $2\text{H}_3\text{PO}_4$, $3\text{H}_3\text{PO}_4$, and $4\text{H}_3\text{PO}_4$ respectively, according to the concentration of the acid, and pyrophosphoric acid compounds containing $3\text{H}_4\text{P}_2\text{O}_7$ or $7\text{H}_4\text{P}_2\text{O}_7$. By heating either of the two latter compounds with a 0.2 or a 0.5 per cent. solution of pyrophosphoric acid, the compounds $\text{Alb}, 4\text{H}_3\text{PO}_4$ or $\text{Alb}, 5\text{H}_3\text{PO}_4$ are formed respectively. The albumin obtained by evaporating dialysed albumin in a vacuum or by coagulating it at 100° and finally drying at 100° in a stream of hydrogen, has properties which differ from those of the albumin prepared by precipitating with alcohol and ether and drying in a similar manner, although both have the composition given above. E. W. W.

Solubility of Serum-Globulin in Water. By EMIL MARCUS (*Zeit. physiol. Chem.*, 1899, 28, 559—575).—Doubt is cast on the hitherto accepted fact that serum-globulin is insoluble in water. It was prepared by several methods from serum and subjected to dialysis; only a small quantity of the globulin was precipitated. The globulin so precipitated and that which remains in solution do not, however, differ in elementary composition, coagulation-temperature, or specific rotatory power. W. D. H.

Spectroscopy of the Blood. By V. ARNOLD (*Chem. Centr.*, 1899, ii, 344; from *Centr. med. Wiss.*, 37, 465—468).—The rose-red solution of hæmatoporphyrin in alcohol or chloroform turns violet on adding bromine water. On adding strong hydrochloric acid, the solution becomes steel-blue. When mixed with aqueous caustic potash, a brown colour is obtained; on adding excess of bromine water, the mixture turns a dirty green, and when hydrochloric acid is added in excess a pure green is obtained. Measurements are given of the bands contained in the absorption spectra of these various solutions.

L. DE K.

Extractives of Muscle. By MAX SIEGFRIED (*Zeit. physiol. Chem.*, 1899, 28, 524—529).—The N:P ratio in various preparations of carniferrin varies considerably according to the method of preparation.

This is due to varying amounts of impurity, of which the principal constituent is an albumose-like substance. W. D. H.

Nucleons. By TH. RICHARD KRÜGER (*Zeit. physiol. Chem.*, 1899, 28, 530—534).—By 'salting-out' solutions of muscle nucleon by sodium chloride or magnesium sulphate, the amount of nitrogen is diminished slightly. If ammonium sulphate is used, the phosphorus is lessened also, and the N:P ratio sinks. These results show that decomposition occurs. A corresponding effect is produced by peptic and tryptic digestion. Similar experiments with milk nucleon gave the same results, except that peptic digestion produces no change and ammonium sulphate causes little or no precipitation.

W. D. H.

Plasmic Acid. By ALBERTO ASCOLI (*Zeit. physiol. Chem.*, 1899, 28, 426—438).—This substance was originally prepared from yeast nuclein by Kossel (*Abstr.*, 1893, i, 680), and differs in many of its characters from nucleic acid. It is now shown to be metaphosphoric acid. As prepared, however, it contains about 1 per cent. of iron, although whether this is to be regarded as 'organic' or 'masked' iron is uncertain, the various colour reactions giving contradictory results.

W. D. H.

Properties of Gelatin. By CARL THORE MÖRNER (*Zeit. physiol. Chem.*, 1899, 28, 471—523).—By treating gelatin in succession with water, dilute potash, dilute acetic acid, water, alcohol, and warm water, filtering, precipitating with alcohol, drying, powdering, extracting with ether, &c., a product was obtained containing only from 0.25 to 0.75 per cent. of ash. It contains 0.2 per cent. of sulphur; this is present in the gelatin, not in impurities; the higher percentage of sulphur given by others is due to proteid admixture. With Millon's reagent, it gives a reaction which, however, is transitory unless the reagent is considerably diluted with water. With sodium chloride, potassium ferrocyanide, and acetic acid, it gives a precipitate when these reagents are present in suitable proportions. The idea that gelatinisation depends on the presence of mineral constituents was not confirmed; neither was any support found for what Dastre calls the 'salt-digestion' of gelatin.

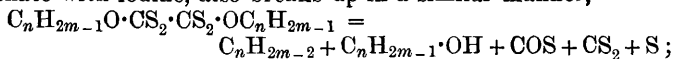
W. D. H.

Cystin, a Decomposition Product of Keratin. By KARL A. H. MÖRNER (*Zeit. physiol. Chem.*, 1899, 28, 595—615).—Horn was treated on the water-bath with 25 per cent. hydrochloric acid for several days; among the products of decomposition (tyrosine, &c.) separated out, most interest attaches to the presence of cystin, 11 grams of which were obtained from 450 grams of dry keratin; cystein was also obtained. In another experiment, more cystin was obtained in proportion, but no cystein.

W. D. H.

Organic Chemistry.

New Method of Preparing Unsaturated Hydrocarbons. By L. TSCHUGAEFF (*Ber.*, 1899, 32, 3332—3335).—When an alkyl xanthate of the unsaturated hydrocarbon radicle C_nH_{2m-1} is subjected to dry distillation, it breaks up in accordance with the following equations, $C_nH_{2m-1}O\cdot CS\cdot SR = C_nH_{2m-2} + COS + RSH$ and $C_nH_{2m-1}O\cdot CS\cdot SR = C_nH_{2m-2} + CS_2 + ROH$. In both reactions the unsaturated hydrocarbon is obtained, and the yield is usually very good. The dioxanthate, produced by the condensation of a metallic xanthate with iodine, also breaks up in a similar manner,



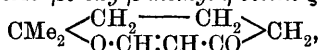
the yield in this case, however, is smaller and the product less pure. These two synthetical methods have been successively employed for the preparation of menthene. Menthol, dissolved in dry toluene, is successively treated with sodium, carbon disulphide, and methyl iodide; the xanthate thus produced, on distillation, yields menthene and methyl mercaptan. The hydrocarbon is purified by fractionation and distillation over sodium; its specific gravity and boiling point correspond with those of other preparations, but its specific rotatory power is far greater; in menthene from the xanthate, $[\alpha]_D$ varies from 114.77° to 116.06° , whilst in the specimen from the dioxanthate it is 111.56° . The nitrosyl chloride of the most active menthene melts at 127° and gives $[\alpha]_D$ 242.5° . The menthene prepared by Urban and Kremers has a specific rotation of 32.77° ; its nitrosyl chloride melts at 128° and has $[\alpha]_D$ 13.76° (compare Abstr., 1894, i, 468).

G. T. M.

Biochemical Oxidation of Propylene Glycol. By ANDRÉ KLING (*Compt. rend.*, 1899, 129, 1252—1254. Compare Abstr., 1899, i, 323).—The aldehydic substance produced by the action of the sorbose bacterium on solutions of propylene glycol is shown to be acetol by isolating it in the form of its oxime. The amount of the glycol oxidised never exceeds 50 per cent. of the total quantity, however long the fermentation is continued; this may be due either to the paralysing effect of the acetol on the bacterium, or to the organism's preference for one of the optical forms of the glycol, or to a combination of the two causes. The unaltered propylene glycol is optically active and appears to consist of a mixture of the dextrorotatory form and the racemic compound. Le Bel, who also effected a partial resolution of propylene glycol by the action of various ferments and moulds, found that the solutions generally became levorotatory. G. T. M.

Cyclic Isomeric Change of Methyloctadienonol. By GEORGES LÉSER (*Bull. Soc. Chim.*, 1899, [iii], 21, 969—973. Compare Abstr., 1899, i, 743).—Methyloctadienonol, the product of the condensation of methylheptenone with ethyl formate, has the constitution $CM_e_2\cdot CH\cdot CH_2\cdot CH_2\cdot CO\cdot CH\cdot CH\cdot OH$, as is shown by its behaviour

towards methylaniline (Abstr., 1899, i, 415) and by its yielding a *monoacetate*, a colourless, odourless liquid boiling at 138° under 13 mm. pressure. When heated for a few minutes at 100° with five times its weight of 80 per cent. sulphuric acid, methyloctadienonol is converted into the isomeric *βθ-oxy-β-methyl-η-octene-ζ-one*,



which melts at about -2.5° and boils without decomposition at 225—227°; it is insoluble in cold alkalis, gives no coloration with ferric chloride, and is not acted on by chromic acid mixture, but immediately decolorises bromine or potassium permanganate solution. It forms an *oxime* melting at 90—91° and boiling at 150—151° under 18 mm. pressure, which yields an *acetyl* derivative boiling at 158—160° under 20 mm. pressure; oxidation with 2 per cent. potassium permanganate solution converts it into the lactone of *γ*-hydroxy-isohexanoic acid. The constitution which has been assigned above to the isomeride of methyloctadienonol is fully confirmed by these reactions, and also by a determination of its molecular refraction (found, 44.02; calculated, 43.95). N. L.

Methylene Sulphate or Sulphuric Methylal. By MARCEL DELÉPINE (*Compt. rend.*, 1899, 129, 831—833).—Methylene sulphate or sulphuric methylal, $\text{CH}_2 \begin{array}{c} \text{O} \\ \diagdown \quad \diagup \\ \text{O} \end{array} \text{SO}_2$ or $\text{CH}_2\text{O}, \text{SO}_3$, obtained by dissolving trioxymethylene in fuming sulphuric acid, is a white, crystalline, odourless, and tasteless substance, almost insoluble in water and organic solvents with the exception of acetone, from which it can be crystallised and from which it is precipitated by adding water, alcohol, ether, or chloroform. It melts at about 155°, but even below this temperature decomposes into sulphur dioxide, carbonic oxide, sulphuric acid, and formaldehyde; in sealed tubes at 200°, it yields the same products together with carbon dioxide and a black, solid $n\text{C}_5\text{H}_6\text{O}$. Methylene sulphate immediately converts aldehyde into paraldehyde; it is but slightly affected by water or alkalis at the ordinary temperature, but at 60—70° is rapidly hydrolysed, yielding formaldehyde and sulphuric acid. Although it has no action on alcohols in the cold, it reacts at 60—70° with methyl, ethyl, propyl, isopropyl, isobutyl, isoamyl, and benzyl alcohols, yielding the corresponding formals and acid sulphates of the various radicles.

The heat of combustion of methylene sulphate (1 gram) is 1286.5 cal.; molecular heat of combustion at constant pressure and volume, 141.5 Cal. Hence $\text{S(oct.)} + \text{O}_4 + \text{C} + \text{H}_2 = \text{SO}_4\text{CH}_2$ solid, develops +162.9 Cals., and the formation of the compound from sulphur trioxide and trioxymethylene develops +18.7 Cals. This reaction is also exothermic if sulphuric acid is substituted for the oxide, owing to the heat of combination of the excess of acid with the water that is formed. C. H. B.

Velocity and Limits of the Esterification of Phosphoric Acid by Glycerol. By HENRI IMBERT and GUILLAME BELUGOU (*Bull. Soc. Chim.*, 1899, [iii], 21, 935—939. Compare Abstr., 1899, i, 659).—When phosphoric acid and anhydrous glycerol are mixed in molecular

proportion, monoglycerophosphoric acid alone is formed, the coefficient of esterification reaching its maximum value almost immediately at the ordinary temperature, and then slowly diminishing. At a higher temperature (105°), the diminution is more rapid, a minimum value being soon reached, after which the coefficient of esterification increases, and ultimately exceeds its original value. The presence of water greatly diminishes the rate of esterification, only 9.32 per cent. of the monohydrated acid being transformed after 13 days at 50° . The action of glycerol on phosphoric oxide results in the formation of each of the three glycerophosphoric acids. N. L.

Acid Esters of Boric Acid. By ALFRED WOHL and C. NEUBERG (*Ber.*, 1899, 32, 3488—3492).—Hydroxychloropropionacetal, $\text{OH}\cdot\text{CH}_2\cdot\text{CHCl}\cdot\text{CH}(\text{OEt})_2$, is obtained by treating acraldehydeacetal with bleaching powder and boric acid in aqueous solution (*Abstr.*, 1898, i, 556); when an attempt is made to prepare glyceraldehydeacetal by boiling the resulting solution with potassium carbonate, ether extracts from the product a *potassium* salt of the composition $\text{OK}\cdot\text{B}[\text{O}\cdot\text{CH}(\text{CH}_2\cdot\text{OH})\cdot\text{CH}(\text{OEt})_2]_2$.

By treating allyl alcohol with calcium hypobromite and boric acid, β -bromohydrin, melting at $227\text{--}230^{\circ}$, was obtained in very small yield; by boiling it with aqueous potassium carbonate and boric acid, and extracting the product with ether, a *potassium* salt, $\text{OK}\cdot\text{B}[\text{O}\cdot\text{CH}(\text{CH}_2\cdot\text{OH})_2]_2$, was obtained.

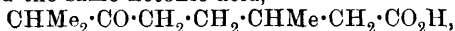
β -Bromohydrin α -ethyl ether appears to react in a similar way; it is made by acting on sodium allyl oxide with ethyl bromide, and treating the product with hypobromous acid. Compounds which do not contain a secondary halogen atom, such as ethyl bromide, benzyl chloride, or the chlorohydrin $\text{CH}_2\text{Cl}\cdot\text{CH}(\text{OH})\cdot\text{CH}_2\cdot\text{OH}$, do not form salts of the kind described, neither do simple secondary halogen derivatives, such as isopropyl chloride and bromide. C. F. B.

α -Dimethylisocrotonic (2-Dimethyl-3-butinoic) Acid. By LOUIS BOUVEAULT (*Bull. Soc. Chim.*, 1899, [iii], 21, 1062—1065).—The action of acetaldehyde on ethyl bromoisobutyrate in the presence of zinc, according to Saytzeff and Reformatsky's process, results principally in the formation of *ethyl β -hydroxy- α -dimethylbutyrate*, but symmetrical *diethyl pentamethylglutarate*, $\text{CHMe}(\text{CMe}_2\cdot\text{CO}_2\text{Et})_2$, is also produced. The latter boils at $170\text{--}180^{\circ}$ under 18 mm. pressure, and has a sp. gr. 0.9953 at 0° . Ethyl β -hydroxy- α -dimethylbutyrate is a colourless liquid which boils at $93\text{--}94^{\circ}$ under 18 mm. pressure and has a sp. gr. 0.9974 at 0° ; it is not affected by most dehydrating agents, but when heated at 100° with phosphorus pentachloride yields *ethyl β -chloro- α -dimethylbutyrate*, which boils at about 200° and is not decomposed by alcoholic potash, and *ethyl α -dimethylisocrotonate*, a colourless liquid boiling at $144\text{--}146^{\circ}$, which differs from the alkyl salts of $\alpha\beta$ -unsaturated acids in not reacting with ethyl sodiomalonate. *α -Dimethylisocrotonic acid*, obtained by hydrolysing its ethyl salt, is a colourless liquid which boils at 92° under 23 mm. pressure and readily combines with bromine to form a crystalline additive *product* melting at 91° . The chloride of this acid reacts with tetrachloroquinol to form two compounds, of the composition $\text{OH}\cdot\text{C}_6\text{Cl}_4\cdot\text{CO}_2\cdot\text{C}_5\text{H}_9$ and

$C_6Cl_4(CO_2 \cdot C_5H_9)_2$ respectively; the former crystallises in white needles, melts at 132° , and is very soluble in neutral solvents, whilst the latter melts at $133-134^\circ$ and is only slightly soluble in neutral solvents. N. L.

Ethyl Acetoacetate. By HEINRICH GOLDSCHMIDT and LAZAR OSLAN (*Ber.*, 1899, 32, 3390—3399).—The hydrolysis of ethyl acetoacetate by sodium hydroxide proceeds as a reaction of the first, and not of the second, order, the velocity constant being independent of the concentration of the ester and of the base. This result can be explained if (1) ethyl acetoacetate is a strong monobasic acid and is converted almost completely into the sodium derivative by an equivalent of sodium hydroxide, whilst (2) sodium acetoacetate possesses no marked acid properties, and (3) if the hydrolysis takes place by the action of the free alkali on the free ester and not on its sodium derivative. The last statement is supported by Fischer's observation that metallic compounds of esters are hydrolysed only with difficulty (*Abstr.*, 1899, i, 262), and especially that ethyl acetoacetate is hydrolysed more slowly than ethyl dimethylacetoacetate, which does not form a metallic derivative. The neutral character of sodium acetoacetate is shown by the fact that it does not produce any marked decrease in the velocity of hydrolysis of ethyl acetate by sodium hydroxide. The acid character of ethyl acetoacetate is shown by conductivity determinations which gave μ_{16} 0.36 and μ_{1024} 3.12, μ_∞ 360, κ 0.63×10^{-7} at 25° ; the ester is thus a much stronger acid than phenol, and slightly stronger than *o*-cresol. The hydrolytic constant of ethyl sodioacetoacetate is calculated to be $\kappa = 2 \times 10^{-7}$ and the small extent of the dissociation is confirmed by cryoscopic measurements. T. M. L.

Orientation in the Terpene Series. XXIV. By ADOLF VON BAEYER (*Ber.*, 1899, 32, 3619—3624) [with OTTO SEUFFERT].—Although $\beta\zeta$ -dimethyloctane- ϵ -oic acid contains its hydroxyl group in the ϵ -position relatively to the carboxyl group, it behaves like a γ - or δ -hydroxy-acid and yields a lactone, $\beta\zeta$ -dimethyloctane- ϵ -olide, $CHMe \cdot CH_2 \cdot CO \cdot CH_2 \cdot CH_2 \cdot CHPr^s > O$, produced when the corresponding hydroxy-acid (*Abstr.*, 1896, i, 217) is heated in a vacuum, distils at $128-130^\circ$ under 17 mm. pressure; when cooled in a freezing mixture, it becomes solid, and as the temperature of the mass rises one portion melts, whilst the residue remains solid in the form of tabular crystals which melt at 47° . Analysis indicates that the two fractions are isomeric; both modifications are insoluble in water and cold dilute caustic soda solution; they dissolve in the hot alkali, but are not attacked by potassium permanganate. The lactone melting at 47° yields an acid melting at 65° , whilst that of lower melting point yields an oily acid. The isomerism of the lactones and their acids depends on the presence of two asymmetric carbon atoms in the molecule of the hydroxy-acid, $CHMe_2 \cdot CH(OH) \cdot CH_2 \cdot CH_2 \cdot CHMe \cdot CH_2 \cdot CO_2H$; one of these is suppressed by oxidation, and accordingly both modifications of this compound yield the same ketonic acid,

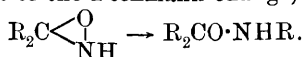


on treatment with potassium dichromate and sulphuric acid; the ketone is identified by means of the oxime which melts at 97°.

G. T. M.

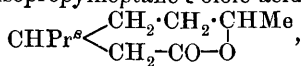
Action of Caro's Reagent on Ketones. By ADOLF VON BAEYER and VICTOR VILLIGER (*Ber.*, 1899, 32, 3625—3633. Compare Caro, *Zeit. angew. Chem.*, 1898, 845).—When Caro's reagent (potassium persulphate and sulphuric acid) acts on a ketone, an oxygen atom is introduced into the molecule between the carboxyl group and one of the hydrocarbon residues; if it is assumed that the first product is a

peroxide, then the course of the reaction $R_2C \begin{smallmatrix} O \\ \diagup \diagdown \end{smallmatrix} \rightarrow R \cdot CO \cdot OR$ is comparable with that of the Beckmann change,



When menthone is treated with a mixture of persulphate and concentrated sulphuric acid, the ϵ -lactone of $\beta\zeta$ -dimethyloctane- ϵ -olonic acid is produced (compare preceding abstract).

The ϵ -lactone of β -isopropylheptane- ϵ -olonic acid,



prepared from tetrahydrocarvone in a similar manner, is an oil boiling at 155—156° under 21 mm. pressure. On hydrolysis, the lactone yields an uncrystallisable hydroxy-acid, the silver salt of which crystallises in white needles; this acid, when treated with Beckmann's mixture, yields a ketonic acid identical with that obtained by direct oxidation from tetrahydrocarvone (*Abstr.*, 1896, i, 217).

Campholide is produced when a benzene solution of camphor is added to a mixture of potassium persulphate, sulphuric acid, and water (H_2SO_4, H_2O), and is isolated by means of its additive compound with hydrogen bromide. The latter compound, *bromocampholic acid*, crystallises in plates and melts at 177°. The campholide is identical with that obtained by Haller from camphoric anhydride. The compound $C_{10}H_{16}O_4$ is obtained as a bye-product in the above reaction; it crystallises from water in plates and melts at 189—190°.

A compound having the composition of acetone peroxide is obtained from acetone and persulphuric acid; it crystallises in prisms, melts at 132—133°, and closely resembles the acetone peroxide obtained by Wolfenstein from acetone and hydrogen peroxide; the latter, however, melts at 94—95° (*Abstr.*, 1895, i, 644).

Terpineol, when treated with Caro's reagent, yields trihydroxy-hexahydrocymene.

G. T. M.

Action of Aluminium Chloride on Camphoric Anhydride. By G. BLANC (*Compt. rend.*, 1899, 129, 1019—1020. Compare Lees and Perkin, *Proc.*, 1898, 14, 111; 1899, 15, 23; 1900, 16, 18).—When the bye-product obtained in the preparation of isolaunonic acid by the action of aluminium chloride on camphoric anhydride is distilled in a vacuum, the distillate consists of unchanged camphoric anhydride, isolaunonic acid, and an oily liquid boiling at 140—145° under 20 mm. pressure. This oily liquid, by repeated extraction with potassium hydrogen carbonate, is separated into an acid portion (A) and a neutral portion (B).

The acid portion (*A*) boils at 140—142° under 20 mm. pressure, and consists of a mixture of several acids of the composition $C_9H_{14}O_2$ and $C_9H_{16}O_2$. It was oxidised with alkaline potassium permanganate and the oxidation product distilled in steam. The residue in the flask consists of the products of oxidation of isolauroic and isolauroic acids, and an oily, non-ketonic acid which is unsaturated and probably has the composition $C_9H_{14}O_2$. The distillate consists of two saturated acids, $C_9H_{16}O_2$; the first melts at 76—77° and forms an amide crystallising in needles and melting at 190°, and a bromoethyl ester, boiling at 130—132° under 25 mm. pressure, which, when treated with alcoholic potash, gives an acid, $C_9H_{14}O_2$, melting at 108—110°, the amide of which melts at 163°. The second acid found in the distillate is an uncrystallisable oil of high boiling point possessing a fatty acid odour; its amide is a liquid.

The neutral portion (*B*) is probably the lactone of an acid, $C_9H_{16}O_3$; it boils at 125—135° under 30 mm. pressure, is insoluble in cold dilute alkalis, but dissolves on warming, and on analysis gives numbers corresponding with the formula $C_9H_{14}O_2$. H. R. LE S.

Camphenilanaldehyde and Camphenilanic Acid. By JULIUS BREIT and WILHELM JAGELKI (*Annalen*, 1899, 310, 112—134. Compare Abstr., 1898, i, 264).—It has been shown by Étard (Abstr., 1893, i, 360) that camphene forms the additive compound $C_{10}H_{16}, 2CrO_2Cl_2$ when dissolved in carbon disulphide and treated with chromyl dichloride; treatment with water gives rise to an aldehyde, to which he ascribed the formula $C_{10}H_{14}O$, calling it camphenaldehyde, and this, on exposure to air, yields the corresponding acid, which was called camphenic acid. The authors, however, find that the aldehyde has the formula $C_{10}H_{16}O$, and they use the name camphenilanaldehyde; the acid $C_{10}H_{16}O_2$ is now called camphenilanic acid.

The double compound, $C_{10}H_{16}, 2CrO_2Cl_2$, is a pale brown powder which is very hygroscopic, forming a green liquid when exposed to air; it tastes sweet, and is somewhat soluble in ether, being insoluble in benzene, petroleum, or carbon tetrachloride.

Camphenilanaldehyde, $\begin{array}{c} CH_2 \cdot CH \\ | \\ CH_2 \cdot CMe_2 \end{array} \begin{array}{c} \diagup \\ >CMe_2 \\ \diagdown \end{array} CH \cdot CHO$, produced by the

action of water on the double compound of camphene with chromyl dichloride, has an agreeable odour, and dissolves readily in organic solvents; it melts at about 70°, and boils at 96° under 14 mm. pressure.

Camphenilanic acid, $\begin{array}{c} CH_2 \cdot CH \\ | \\ CH_2 \cdot CMe_2 \end{array} \begin{array}{c} \diagup \\ >CMe_2 \\ \diagdown \end{array} CH \cdot CO_2H$, melts at 65° and

boils at 147° under 14 mm. pressure; the calcium and silver salts are crystalline and anhydrous. The chloride, $C_{10}H_{15}OCl$, boils at 105—106° under 14 mm. pressure, and the methyl ester boils at 99—100° under 12 mm. pressure.

Bromocamphenilanic acid, $C_{10}H_{15}O_2Br$, separates from petroleum in colourless crystals and melts at 145°; the chloride, prepared by the action of bromine on camphenilanic chloride, is a white, crystalline substance, and boils at 165° under 14 mm. pressure.

Isocamphenilanic acid, $C_{10}H_{16}O_2$, prepared by heating camphenilanic

acid with dilute nitric acid, melts at 118° , and separates from petroleum in crystals belonging to the triclinic system; [$a:b:c = 1.8852:1:1.2155$; $\alpha = 69^{\circ}3'30''$, $\beta = 99^{\circ}20'$, $\gamma = 99^{\circ}0'30''$]. It is also produced on oxidising camphenilanaldehyde with potassium permanganate; the *calcium* salt contains $2H_2O$, and the *silver* salt resists the action of light.

Hydroxycamphenilanic (*campheniloloic*) acid, $C_{10}H_{16}O_3$, prepared by heating bromocamphenilanic acid with sodium carbonate, melts at $170-172^{\circ}$; the *sodium* salt is not readily soluble in cold water, and the *silver* salt is crystalline.

It is probable that camphenilanaldehyde is identical with the aldehydic substance obtained by Wagner from camphene glycol and hydrochloric acid, and hydroxycamphenilanic acid is most likely identical with the acid obtained by Wagner on oxidising camphene with potassium permanganate (compare also Jagelki, *Abstr.*, 1899, i, 627). M. O. F.

Preparation of Azelaic Acid. By LÉON MAQUENNE (*Bull. Soc. Chim.*, 1899, [iii], 21, 1061—1062).—Azelaic acid is usually obtained by oxidising castor oil with nitric acid, but a purer product and a larger yield are more readily obtained by the action of potassium permanganate on an alkaline solution of the crude ricinoleic acid obtained by the hydrolysis of the oil. N. L.

Malic Acid from Hippophæ Rhamnoides. By HUGO ERDMANN (*Ber.*, 1899, 32, 3351—3354. Compare this vol., i, 10).—The malic acid obtained from the ripe berries of *Hippophæ rhamnoides* (Seabuckthorn) is identical with that isolated from mountain ash berries; their ammonium salts have the same molecular rotation ($2.89-2.94^{\circ}$)

Calcium malate separates from hot aqueous solutions in crystals containing $1\frac{1}{2}H_2O$. The berries also contain other acidic substances and mannitol, the latter being isolated in the form of its calcium derivative. G. T. M.

Some Complex Salts of Tartaric and Malic Acids, and their Specific Rotatory Power. By ARTHUR ROSENHEIM and HERRMANN ITZIG (*Ber.*, 1899, 32, 3424—3440).—The potassium, sodium, and ammonium “diberylliumtartrates,” $M'_2O, 4BeO, 2C_4H_4O_6$, previously described (*Abstr.*, 1898, ii, 71) have been examined as regards their optical activity; the specimens prepared contained respectively 6, 9, and $9H_2O$. The molecular rotation, $[M]_D$, at 20° in aqueous solution, is about 225° , 225° , and 242° respectively, and varies but little with the dilution; it is due to a complex anion, $(C_8H_4O_{13}Be_4)''$ or $(C_4H_3O_7Be_2)''_2$, of the nature $(-CO_2 \cdot [C_2H_2 \cdot O_2Be] \cdot CO_2 \cdot Be)_2O$ or $-CO_2 \cdot [C_2H_2 \cdot O_2Be] \cdot CO_2 \cdot Be \cdot OH$,

and exceedingly stable, since dilution does not affect the rotation and so cannot produce hydrolysis. Potassium and ammonium “monoberylliumtartrates,” $M'_2O, 2BeO, 2C_4H_4O_6 + 2H_2O$ (*loc. cit.*, 72), were examined in the same way (the *sodium* salt, with $3H_2O$, could not be obtained sufficiently pure); the molecular rotation at 20° was about 125° and 126° respectively, and varied but little with the dilution; it was probably due to a stable complex anion, $(C_8H_8O_{13}Be_2)''$, of the nature $(-CO_2 \cdot [CH \cdot OH]_2 \cdot CO_2 \cdot Be)_2O$. By dissolving an equivalent

amount of beryllium hydroxide in a boiling solution of tartaric acid, a *beryllium tartrate*, $C_4H_2O_7Be_3 + 7H_2O$, was obtained; this has, at 20° , a molecular rotation of about 171° in 3 per cent. solution, increasing with the dilution. In all cases, the entrance of beryllium into the molecule causes a great increase in the rotatory power. *Ammonium di- and mono-beryllium racemates* were also prepared; they have the same composition as the *d*-tartrates; but they are optically inactive, so that the *l*-tartrate molecule must have been affected in the same degree as the *d*-molecule, and in the opposite sense, by the entrance of the beryllium.

Similar observations were made in the case of malic acid. *Potassium, sodium, and ammonium diberylliummalates*, $M'_2O, 4BeO, (C_4H_3O_3)_2O$, with 5, 7, and $4H_2O$ respectively, were prepared by saturating boiling aqueous solutions of the alkali-hydrogen malate with freshly precipitated beryllium hydroxide. The molecular rotation is about -199° at 16° , -202° at 16° , and -201° at 13° respectively, and is due to an anion of the nature $-CO_2 \cdot CH_2 \cdot CH < \begin{smallmatrix} O \cdot Be - O - Be \cdot O \\ CO_2 \cdot Be \cdot O \cdot Be \cdot CO_2 \end{smallmatrix} > CH \cdot CH_2 \cdot CO_2^-$.

Ammonium monoberylliummalate, $(NH_4)_2O, 2BeO, 2C_4H_4O_4 + H_2O$, prepared like the analogous tartrate, has a molecular rotation of about -106° at 20° .

By adding beryllium sulphate and sodium hydroxide in varying proportions to solutions of tartaric or malic acids, the molecular rotation reached a maximum when the proportions corresponded with the formation of the "diberyllium" salt, and was then about equal to that of the pure salt. Ethyl hydrogen tartrate gave a maximum rotation when the proportions were $C_6H_{10}O_6, 2BeSO_4, 4KOH$. The rotatory power of quinic and *d*-chlorosuccinic acids, which contain no alcoholic hydroxyl groups, is not affected by the addition of beryllium sulphate (and alkali); nor is that of dextrose.

Neither magnesium, zinc, nor cadmium forms complex tartrates or malates like those formed by beryllium, nor do their salts affect the rotatory power of alkaline tartrates or malates. C. F. B.

Action of Nitric Acid on Acids of the Fatty Series which contain the Isopropyl Group. By JULIUS BREDT and J. B. C. KERSHAW (*Ber.*, 1899, 32, 3661—3666. Compare Abstr., 1883, 176).—The experiments of the authors have been extended to dibasic acids which have been found to behave in a similar manner to the monobasic acids which had been previously examined.

Terebic acid is converted by the continued action of nitric acid into γ -valerolactone- $\beta\gamma$ -dicarboxylic acid, $CH_2 < \begin{smallmatrix} CH(CO_2H) \\ CO - O \end{smallmatrix} > CMe \cdot CO_2H$, which has already been prepared by Rach (Abstr., 1886, 1012). The *diethyl* ester boils at 174 — 175° under 9 mm. pressure. Isopropylsuccinic acid (pimelic acid) is also converted by nitric acid into valerolactonedicarboxylic acid. These two compounds therefore behave in a precisely similar manner to isohexoic acid and isohexolactone. A. H.

Natural Cyclic Isomeric Change of Citronellal. By HENRI LABBÉ (*Bull. Soc. Chim.*, 1899, [iii], 21, 1023—1025. Compare Abstr., 1899, i, 622).—Pure citronellal is very unstable, and upon

taneously undergoes the same isomeric change which is effected more rapidly by the action of acids. A specimen which had been kept for two months was found to be almost entirely converted into isopulegol, which was identified by oxidising it with chromic acid mixture, and converting the isopulegone thus formed into the mixture of two isomeric semicarbazones which is characteristic of this substance. In the presence of hydrocarbons and terpenylic alcohols, such as occur in commercial specimens, citronellal is much more stable.

N. L.

Formation of Barium Citryl and Citronellyl Sulphites. By HENRI LABBÉ (*Bull. Soc. Chim.*, 1899, [iii], 21, 1026—1027).—In reply to the remarks of Tiemann (*Abstr.*, 1899, i, 622), the author states that it is not contended that an accurate quantitative separation of citral from citronellal can be effected by the process described by Flatau and Labbé (*loc. cit.*). The barium hydrogen sulphite compound of citronellal is precipitated immediately to the extent of about 85 per cent. of the theoretical amount, whilst the yield of the corresponding citral derivative never exceeds 27—28 per cent., and in the first five minutes only amounts to 17—18 per cent. The citral compound, moreover, is contaminated with barium sulphite, whereas the citronellal derivative is precipitated in a pure state.

N. L.

Derivatives of the Isuretine of Formhydroxamic Acid and their Relation to Fulminic Acid. By H. C. BIDDLE (*Annalen*, 1899, 310, 1—24. Compare Nef, *Abstr.*, 1896, i, 71).—*Ethylisuretine*, $\text{NH}_2\cdot\text{CH}\cdot\text{NOEt}$, has been described already as ethoxyformamidine (Nef, *Abstr.*, 1895, i, 12).

Benzylisuretine, $\text{NH}_2\cdot\text{CH}\cdot\text{NO}\cdot\text{CH}_2\text{Ph}$, prepared from isuretine by the action of benzyl chloride and alcoholic potash, crystallises from petroleum in slender needles and melts at 58° ; hot concentrated hydrochloric acid eliminates α -benzylhydroxylamine, and nitrous acid gives rise to a variety of products, including benzaldehyde, benzyl alcohol, and benzylchloro-formoxime. The *platinichloride* crystallises in yellow, rhombic plates and melts at 157 — 158° .

Methylisuretine, $\text{NH}_2\cdot\text{CH}\cdot\text{NOME}$, crystallises from light petroleum in plates and melts at 40 — 40.5° .

An attempt to prepare the benzyl derivative of fulminic acid by the action of chloroform and alcoholic potash on α -benzylhydroxylamine gave rise to the compound $\text{C}_8\text{H}_9\text{O}_2\text{N}$, which crystallises from petroleum in colourless leaflets and melts at 86 — 86.5° ; a mixture of benzyl alcohol and benzyl ether is also produced, along with a substance having the odour of an isonitrile.

Benzylformhydroxamic acid, $\text{CH}_2\text{Ph}\cdot\text{O}\cdot\text{NH}\cdot\text{CHO}$, obtained by heating α -benzylhydroxylamine with formic acid, is a viscous, colourless oil, which boils at 170° under 15 mm. pressure, when it decomposes slightly; cold, concentrated hydrochloric acid resolves it into formic acid and α -benzylhydroxylamine hydrochloride. The *silver* derivative is amorphous, and yields benzaldehyde when heated.

Benzylchloro-formoxime, $\text{CH}_2\text{Ph}\cdot\text{O}\cdot\text{N}\cdot\text{CHCl}$, produced by the action of phosphorus pentachloride on benzylformhydroxamic acid, is a

colourless liquid having an odour of fir-wood; it boils at 101° under 11 mm. pressure, and at 210° under atmospheric pressure. It is a stable substance, and is devoid of basic properties; hydrochloric acid eliminates α -benzylhydroxylamine quantitatively.

Formhydroxamic acid has been investigated by Jones (Abstr., 1898, i, 173). It displays a great tendency to dissociate into hydroxylamine and carbon monoxide, decomposing in this way when heated a few degrees above the melting point. The solution in acetone undergoes spontaneous change in the course of a few days, yielding acetoxime. The sodium salt decomposes into ammonia and sodium carbonate. The lead salt separates from water in colourless, transparent crystals containing water, and explodes at 145° ; when dried at 100° , it yields ammonia and lead carbonate.

Chloro-formoxime benzoate, $\text{COPh}\cdot\text{O}\cdot\text{N}\cdot\text{CHCl}$, obtained from the benzoate of formhydroxamic acid by the action of phosphorus pentachloride, crystallises from ether in odourless needles and melts at $53\cdot5$ — $54\cdot5^{\circ}$; aniline converts it into benzanilide and chloro-formoxime, the latter yielding phenylisouretine.

Chloro-formoxime acetate, $\text{COMe}\cdot\text{O}\cdot\text{N}\cdot\text{CHCl}$, prepared from the acetate of formhydroxamic acid and phosphorus pentachloride, boils at 60 — 63° under 15 mm. pressure; it has a penetrating odour resembling that of chloro-formoxime, and gives rise to similar physiological effects. When the purified substance is heated with a concentrated aqueous solution of silver nitrate, it is decomposed slowly, yielding silver fulminate, silver chloride, and acetic acid.

Ethyl α -benzyloximinoformic ether, $\text{CH}_2\text{Ph}\cdot\text{O}\cdot\text{N}\cdot\text{CH}\cdot\text{OEt}$, is the more volatile of the two isomerides produced by the action of ethyl iodide on the silver salt of benzylformhydroxamic acid, and boils at 121 — 122° under 15 mm. pressure, having the refractive index n_D $1\cdot5105$; alcoholic hydrochloric acid gives rise to α -benzylhydroxylamine, whilst the gas eliminates ethylic chloride. The β -modification boils at 149 — 150° under 15 mm. pressure, and has n_D $1\cdot5256$; in chemical behaviour, it resembles the isomeride.

α -Benzyloximinoformyl acetyl oxide, $\text{CH}_2\text{Ph}\cdot\text{O}\cdot\text{N}\cdot\text{CH}\cdot\text{OAc}$, prepared from acetylchloride and benzylformhydroxamic acid, melts at 146 — 148° ; the β -modification melts at 95 — 96° , and boils at 162 — 163° under 12 mm. pressure.

Benzyloximinodiacetyl oxide, $\text{CH}_2\text{Ph}\cdot\text{O}\cdot\text{N}\cdot\text{CMe}\cdot\text{OAc}$, results from α -benzylhydroxylamine and acetic anhydride; it crystallises from petroleum in snow-white needles, and melts at 101 — 102° .

Benzyloximinoformyl benzoyl oxide, $\text{CH}_2\text{Ph}\cdot\text{O}\cdot\text{N}\cdot\text{CH}\cdot\text{OBz}$, obtained from silver benzylformhydroximate and benzoyl chloride, crystallises from petroleum in colourless, transparent plates, and melts at $29\cdot5$ — $30\cdot5^{\circ}$; it dissolves readily in organic solvents, and is resolved by acids into α -benzylhydroxylamine and formic and benzoic acids. It is also produced when sodium benzylformhydroxamic acid is treated with benzoyl chloride, β -benzoyl- α -benzylhydroxylamine, $\text{CH}_2\text{Ph}\cdot\text{O}\cdot\text{NHBz}$, being also formed; this crystallises in rhombic plates, and melts at 103 — 104° (compare Beckmann, Abstr., 1894, i, 25).

M. O. F.

Purification of Osazones and Estimation of their Rotatory Power. By CARL NEUBERG (*Ber.*, 1899, 32, 3384—3388).—Practically all osazones are soluble in pyridine, the solubilities of the various members differing but little; as a rule, 1 gram of the solvent dissolves 0.25 gram of an osazone in the cold, and 0.6 gram at the boiling point of the solvent. Most of the osazones may be purified by recrystallisation from a mixture of pyridine and some other suitable solvent, such as water, alcohol, benzene, carbon disulphide, &c., or even more quickly by solution in pyridine and precipitation with benzene, ether, or light petroleum. Hydrazones and hydrazides behave in a similar manner. Solutions of osazones in pyridine or in pyridine and another solvent, especially ethyl alcohol, have been examined polarimetrically. The results obtained differ, not only in amount, but in some cases also in direction, from those given when acetic acid or alcoholic solutions are employed. The following rotations were obtained in a 100 mm. tube by using 0.2 gram of osazone, 4 c.c. of pyridine, and 6 c.c. of ethyl alcohol.

Phenylosazones of *l*-arabinose, $+1^{\circ}10'$; xylose, $-0^{\circ}15'$; rhamnose, $+1^{\circ}24'$; dextrose, $-1^{\circ}30'$; *d*-galactose, $+0^{\circ}48'$; sorbinose, $-0^{\circ}15'$; maltose $+1^{\circ}30'$; lactobiose $\pm 0^{\circ}$; *p*-bromophenylosazones of *l*-arabinose, $+0^{\circ}28'$; xylose, $\pm 0^{\circ}$; dextrose, $-0^{\circ}31'$; *p*-bromophenylhydrazine glycuronate. (*Abstr.*, 1899, i, 933) gave $-7^{\circ}25'$, from which it follows that $[\alpha]_D^{20} = -369^{\circ}$.

Dextrose p-bromophenylosazone, melts at 222° and resembles the phenylosazone; that of *xylose* melts at 208° , and is moderately soluble in most solvents; *l*-arabinose-*p*-bromophenylosazone sinters at 185° , melts at 196 — 200° , and is more readily soluble in ether than the xylose derivative. Most of the parabromophenylosazones crystallise either in the usual yellow needles or in well-developed, six-sided plates.

J. J. S.

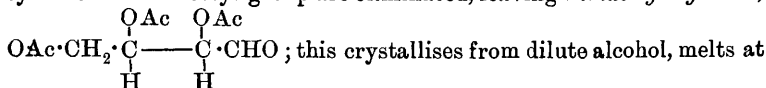
***d*-Erythrose.** By OTTO RUFF [and in part MEUSSER] (*Ber.*, 1899, 32, 3672—3681. Compare *Abstr.*, 1899, i, 324).—Calcium *d*-arabonate, on oxidation with hydrogen peroxide and ferric acetate, yields a mixture rich in *d*-erythrose, which on treatment with phenylbenzylhydrazine gives *d*-erythrophenylbenzylhydrazone; this crystallises in white needles melting at 105.5° , has a specific rotation $[\alpha]_D - 32^{\circ}$ at 20° , and on treatment with a solution of formaldehyde yields *d*-erythrose.

$$\begin{array}{c} \text{OH} \quad \text{OH} \\ | \quad | \\ \text{d-Erythrose, } \text{OH} \cdot \text{CH}_2 \cdot \text{C} - \text{C} \cdot \text{CHO}, \text{ shows mutarotation, and has} \\ | \quad | \\ \text{H} \quad \text{H} \end{array}$$

an approximate maximum specific rotation $[\alpha]_D - 14.5^{\circ}$ at 20° ; it reduces Fehling's solution slightly in the cold, does not ferment, and yields an osazone which crystallises from benzene in the form of yellow needles melting at 164° . On reduction with sodium amalgam, it yields inactive erythritol melting at 120° (corr.). The melting point of the natural inactive erythritol has been stated by Lamy to be 112° and by Liebermann as 126° ; the author finds it to be 120° . The oxidation of calcium *d*-arabonate with bromine gives *d*-erythronic acid. This is separated by means of the *strychnine* or the *brucine* salt, which

melts about 215° and has a specific rotation $[\alpha]_D -23.5^{\circ}$ at 20° . The aqueous solution of the acid, obtained by the decomposition of these salts, turns the plane of polarised light strongly to the left, but on evaporation leaves the *lactone*, which crystallises in the form of compact prisms melting at 103° and has a specific rotation $[\alpha]_D -73.3^{\circ}$ at 20° . The *calcium* salt crystallises with $2H_2O$ and has the specific rotation $[\alpha]_D +8.2^{\circ}$ at 20° . The *phenylhydrazide* forms prismatic leaflets melting at 128° and has the specific rotation $[\alpha]_D +17.5^{\circ}$ at 20° . *d*-Erythronic acid is identical with the trihydroxybutyric acid obtained in the oxidation of *lævulose* (Herzfeld, Börnstein, and Winter, Abstr., 1886, 862). R. H. P.

Degradation of *l*-Arabinose. By ALFRED WOHL (*Ber.*, 1899, 32, 3666—3672. Compare Abstr., 1893, 292, and 1898, i, 168).—The oximation and subsequent acetylation of *l*-arabinose yield the nitrile of *l*-tetracetyl-arabonic acid; from this, by the action of silver oxide suspended in methyl alcohol containing a trace of ammonia, hydrogen cyanide and an acetyl group are eliminated, leaving *l*-triacetylerythrose,



On treatment of the nitrile with silver oxide and ammonia, *l*-erythrosediacetamide is obtained; it crystallises from water, melts and decomposes at 210° , and has a specific rotation $[\alpha]_D -7.9^{\circ}$. On hydrolysis with dilute hydrochloric or sulphuric acid of a solution of the diacetamide, the specific rotation changes to $[\alpha]_D +32.7^{\circ}$, which is probably the specific rotation of *l*-erythrose. The sugar could not be crystallised or otherwise purified, but an *osazone* crystallising from benzene or water and melting at 163 — 164° is easily obtained. Attempts were made to purify the sugar from ammonium carbonate by evaporation in a vacuum, but by this means *l*-dierythroseimide, $NH \left[CH \begin{array}{c} \text{CH(OH)} \\ \diagup \quad \diagdown \\ O \quad CH_2 \end{array} \right]_2 CH \cdot OH$ is obtained, which crystallises from warm water, melts at 155° , exhibits mutarotation, and has a maximum specific rotation $[\alpha]_D +136.3^{\circ}$.

R. H. P.

Resolution of Racemic Compounds into Active Components. By EMIL FISCHER (*Ber.*, 1889, 32, 3617—3619).—The enzyme emulsin hydrolyses the β -methylglucoside of dextrose, but has no action on its optical antipode derived from *l*-glucose; a similar difference is observed when the α -methyl derivatives are treated with yeast enzymes; under these conditions, the racemic compounds are rendered active, one active form being decomposed whilst the other remains unaltered.

The selective action of enzymes is quite analogous to the partial resolution of *r*-mandelic acid by etherification with *l*-menthol (Marckwald and McKenzie, Abstr., 1899, ii, 733, and Walden, this vol., i, 7). Both processes are similar in principle to the method involving the employment of micro-organisms, but owing to the

substitution of the living cell by an enzyme or by some other asymmetric compound, the phenomenon now becomes a chemical one.

G. T. M.

Action of Acetic Anhydride on Cellulose in Presence of Sulphuric Acid. By ANTOINE P. N. FRANCHIMONT (*Rec. Trav. Chim.*, 1899, **18**, 472—476).—A reply to Skraup's note on cellulose (*Abstr.*, 1899, **i**, 852). The cellulose acetate melting at 212° is not identical with inosite hexacetate, which has the same melting point.

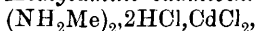
Cellulose acetate is hydrolysed by aqueous ammonia or an ammoniacal solution of cuprous oxide, the cellulose being recovered. It is completely soluble in chloroform, the solution resembling collodion; it also dissolves in acetic acid, and is reprecipitated by the addition of water.

T. H. P.

Alkalimetry of the Amines. By A. ASTRUC (*Compt. rend.*, 1899, **129**, 1021—1023).—The amines of the aliphatic series behave as strong bases towards phenolphthalein and methyl-orange, whereas the amines of the aromatic series are weak bases, being neutral to phenolphthalein and mono-acid towards methyl-orange. Hydroxylamine behaves as an aromatic amine, its hydrochloride in aqueous solution being neutral to methyl-orange and acid to phenolphthalein. The addition of two aliphatic alkyl groups to a primary aromatic amine does not increase its basicity. When a second phenyl group is introduced into a primary aromatic amine, the basicity is lowered, as is shown by diphenylamine, which is neutral to both phenolphthalein and methyl-orange.

H. R. LE S.

Double Halogen Salts of Cadmium with the Methylamines and Tetramethylammonium. By C. D. RAGLAND (*Amer. Chem. J.*, 1899, **22**, 417—434).—*Methylamine cadmiochloride*,



the only double-salt obtainable by mixing solutions of cadmium chloride and methylamine hydrochloride, forms tabular, transparent crystals with a perfect cleavage; of the *bromides*, $\text{NH}_2\text{Me}, \text{HBr}, \text{CdBr}_2$, however, is only isolated with difficulty, and forms long, flattened prisms, whilst $(\text{NH}_2\text{Me})_2, 2\text{HBr}, \text{CdBr}_2$ separates in large, tabular, crystalline masses; no double iodide could be prepared.

Dimethylamine cadmiochlorides.—(1), $\text{NHMe}_2, \text{HCl}, \text{CdCl}_2$, forms long prisms, darkens at 240° , and melts and decomposes at 261 — 262° ; (2), $\text{NHMe}_2, \text{HCl}, 2\text{CdCl}_2 + 2\text{H}_2\text{O}$ crystallises similarly and does not melt or decompose at 270° ; (3), $(\text{NHMe}_2)_3, 3\text{HCl}, 2\text{CdCl}_2$, forms flat, transparent prisms. All three salts are easily soluble in water. *Dimethylamine cadmiobromides*.—(1), $\text{NHMe}_2, \text{HBr}, \text{CdBr}_2$ forms slender, white needles or thin prisms; (2), $(\text{NHMe}_2)_2, 2\text{HBr}, \text{CdBr}_2$ crystallises in rhombohedral prisms; (3), $\text{NHMe}_2, \text{HBr}, 4\text{CdBr}_2$ forms short, thick, brilliant crystals. *Dimethylamine cadmioiodide*, $\text{NHMe}_2, \text{HI}, \text{CdI}_2$, forms tabular, cubical crystals.

Trimethylamine cadmiochlorides.—(1), $\text{NMe}_3, \text{HCl}, \text{CdCl}_2$ has been described by Hiortdahl (*Zeit. Kryst. Min.*, 1882, **6**, 466); (2), $(\text{NMe}_3)_3, 3\text{HCl}, 2\text{CdCl}_2$ crystallises in obliquely terminated, flattened prisms. *Trimethylamine cadmiobromides*.—(1), $\text{NMe}_3, \text{HBr}, \text{CdBr}_2$

(Hiortdahl, *loc. cit.*); (2), $(\text{NMe}_3)_3, 3\text{HBr}, 2\text{CdBr}_2$ forms flattened prisms terminating in pyramidal planes. *Trimethylamine cadmioiodides*.—(1), $\text{NMe}_3, \text{HI}, \text{CdI}_2$, forms large cubes; (2), $(\text{NMe}_3)_2, 2\text{HI}, \text{CdI}_2$, crystallises in beautiful, rhombic prisms.

Tetramethylammonium cadmiochloride, $\text{NMe}_4\text{Cl}, \text{CdCl}_2$, forms hexagonal-pyramidal crystals. *Cadmiochlorides*.—(1), $\text{NMe}_4\text{Br}, \text{CdBr}_2$, forms crystals similar to those of the corresponding double chloride, and is sparingly soluble in water; (2), $(\text{NMe}_4\text{Br})_2, \text{CdBr}_2$, crystallises in short, imperfect, flattened prisms. *Cadmioiodides*.—(1), $\text{NMe}_4\text{I}, \text{CdI}_2$ is a crystalline powder sparingly soluble in water; (2), $(\text{NMe}_4\text{I})_2, \text{CdI}_2$, is more easily soluble, and forms transparent octahedra. W. A. D.

Double Halogen Salts of Tin with Aliphatic Amines and with Tetramethylammonium. By C. G. COOK (*Amer. Chem. J.*, 1899, 22, 435—446. Compare Slagle, *Abstr.*, 1899, i, 39).—The *stannochloride*, $\text{NH}_2\text{Me}, \text{HCl}, \text{SnCl}_2$, of methylamine forms well-defined, transparent prisms, that of *dimethylamine*, $\text{NHMe}_2, \text{HCl}, \text{SnCl}_2$, needle-like crystals, whilst *trimethylamine stannochloride*, $\text{NMe}_3, \text{HCl}, \text{SnCl}_2$, is sparingly soluble in water and crystallises in triangular plates; Hiortdahl's analyses (*Zeit. Kryst. Min.*, 1882, 6, 462) of the stannichlorides of the three bases are confirmed. *Tetramethylammonium stannochloride*, $\text{NMe}_4\text{Cl}, \text{SnCl}_2$, is sparingly soluble in water, and from dilute solutions crystallises in needles; it is easily oxidised by the air to the *stannichloride*, $(\text{NMe}_4\text{Cl})_2, \text{SnCl}_4$, which forms measurable crystals.

Ethylamine stannochloride, $\text{NH}_2\text{Et}, \text{HCl}, \text{SnCl}_2$, forms white needles, and is rapidly oxidised by the air to the *stannichloride*, $(\text{NH}_2\text{Et})_2, \text{H}_2\text{SnCl}_6$, which crystallises in well-defined, pyramidal crystals, possessing little lustre. *Trimethylamine stannochloride* could not be obtained owing to its rapidly oxidising; specimens of the *stannichloride* were prepared which, although apparently homogeneous, were in reality mixtures of the compounds $(\text{NMe}_3)_2, \text{H}_2\text{SnCl}_6$; $\text{NMe}_3, \text{HCl}, \text{SnCl}_4$, and $(\text{NMe}_3)_3, 3\text{HCl}, \text{SnCl}_4$.

Methylamine stannobromide, $\text{NH}_2\text{Me}, \text{HBr}, \text{SnBr}_2$, forms dark-red needles, and the *stannibromide*, $(\text{NH}_2\text{Me})_2, \text{H}_2\text{SnBr}_6$, yellow, crystal masses of varying habit. *Dimethylamine stannobromide*, $\text{NHMe}_2, \text{HBr}, \text{SnBr}_2$, crystallises in beautiful, lustrous, white scales or feathers, and is sparingly soluble in water, whilst the *stannibromide*, $(\text{NHMe}_2)_2, \text{H}_2\text{SnBr}_6$, forms transparent, hexagonal prisms with modified ends. *Trimethylamine stannobromide* could not be prepared owing to its readily oxidising in the air to the *stannibromide*, $(\text{NMe}_3)_2, \text{H}_2\text{SnBr}_6$, which forms small, transparent crystals.

Ethylamine stannobromide, $\text{NH}_2\text{Et}, \text{HBr}, \text{SnBr}_2$, forms yellowish-white, lustrous needles, and the *stannibromide*, $(\text{NH}_2\text{Et})_2, \text{H}_2\text{SnBr}_6$, bright yellow, transparent, pyramidal prisms. *Triethylamine stannobromide* could not be isolated, but the *stannibromide*, $(\text{NEt}_3)_2, \text{H}_2\text{SnBr}_6$, forms yellow, rhombic plates. W. A. D.

Physiological Action of Methylnitramine in Relation to its Chemical Constitution. By G. BELLAAR SPRUYT (*Proc. k. Akad. Wetensch. Amsterdam*, 1899, i, 321—322).—The sodium derivative of methylnitramine has no toxic action on the animal system, and in this respect resembles the nitroparaffins, but differs from the isomeric

nitrites. The physiological behaviour of the substance supports the view of its constitution maintained by Franchimont in opposition to Hantzsch; the former regards it as a nitro-compound (Abstr., 1895, i, 445; compare, however, Abstr., 1897, i, 8; 1898, i, 293), whilst the latter proposes a formula which contains the radicle $\text{:NO}\cdot\text{OH}$ (compare, however, Abstr., 1896, i, 353, 673), and recalls that of the nitrites.

G. T. M.

Preparation of Ethyldichloroamine. By H. PALOMAA (*Ber.*, 1899, 32, 3343—3344. Compare Seliwanoff, Abstr., 1893, i, 192).—Ethyldichloroamine is best prepared by adding a concentrated aqueous solution of ethylamine hydrochloride to dry bleaching powder; the substance thus produced boils at $85\text{--}90^\circ$ and may be kept under water for 18 months without undergoing decomposition.

G. T. M.

Preparation of Ethyldichloroamine. By JOSEPH TCHERNIAC (*Ber.*, 1899, 32, 3582).—The author's method of preparing ethyldichloroamine (Abstr., 1876, i, 913) gives as good results as Palomaa's modification (preceding abstract) of this process; the decomposition of the base on keeping is caused by light and not by the presence of water, and can be prevented by storing in red glass bottles.

W. A. D.

Stereochemistry of Nitrogen [Propylisobutylamine]. By WILHELM MARCKWALD (*Ber.*, 1899, 32, 3508—3510).—*p*-Toluenesulphopropylamide dissolves readily in organic solvents and melts at 52° . *p*-Toluenesulphopropylisobutylamide crystallises from light petroleum and melts at $59\text{--}60^\circ$. Propylisobutylamine boils at 125° under 768 mm. pressure; the hydrochloride melts at 275° and sublimes at a lower temperature; the platinichloride is orange-coloured and melts at $187\text{--}188^\circ$; the aurichloride forms yellow crystals and melts at $187\text{--}188^\circ$.

T. M. L.

Constitution of Lysine. By ALEXANDER ELLINGER (*Ber.*, 1899, 32, 3542—3546).—Drechsel's lysine, obtained from either casein or the peptone from the self-digestion of the pancreas, gives a fairly good yield of pentamethylenediamine (cadaverine) when allowed to undergo putrefaction by the aid of rotting pancreas in an atmosphere of hydrogen. This would indicate that lysine stands in the same relationship to pentamethylenediamine that ornithine does to tetramethylenediamine (Abstr., 1899, i, 186), and is therefore α - ϵ -diaminohexoic acid, $\text{NH}_2\cdot\text{CH}_2\cdot[\text{CH}_2]_3\cdot\text{CH}(\text{NH}_2)\cdot\text{CO}_2\text{H}$.

J. J. S.

Derivatives of Pyrotartaric Acid and of the Isomeric Glutaric Acid. By P. A. MEERBURG (*Rec. Trav. Chim.*, 1899, 18, 367—377).—Pyrotartaric methylamide, $\text{C}_3\text{H}_6(\text{CO}\cdot\text{NHMe})_2$, prepared either from methyl pyrotartrate or from pyrotartaric chloride, is found to have the melting point $164\text{--}165^\circ$; the value $113\text{--}115^\circ$ given by Henry (Abstr., 1885, 886) is hence erroneous.

Pyrotartaric dimethylamide, $\text{C}_3\text{H}_6(\text{CO}\cdot\text{NMe}_2)_2$, prepared by the action of dimethylamine on pyrotartaric chloride, is a colourless liquid boiling at $115\text{--}120^\circ$ under 0.5 to 1 mm. pressure.

Methyl glutarate, $C_3H_6(CO_2Me)_2$, is a colourless liquid with a faint, pleasant odour; it boils at $93.5-94.5^\circ$ under 13 mm. and at $213.5-214^\circ$ under 751.5 mm. pressure. Its specific gravity is 1.09337 at $15^\circ/4^\circ$.

Glutaric methylamide, $C_3H_6(CO \cdot NHMe)_2$, separates by the addition of benzene to its solution in chloroform in large needles melting at 126° ; it is very soluble in water, chloroform, or acetone, less so in benzene, and insoluble in ether or light petroleum.

Glutaric dimethylamide, $C_3H_6(CO \cdot NMe_2)_2$, is deposited from chloroform in large, transparent, lozenge-shaped crystals, which are very hygroscopic; it melts at $49-51^\circ$.

Tables, containing, however, a large number of gaps, are given of the boiling and melting points of derivatives of the acids of the oxalic acid series with odd and even numbers of carbon atoms. The chief regularities shown are as follows: The boiling points of methyl oxalate and succinate differ by 32° , which is also the difference between the values for methyl malonate and glutarate. On replacing a hydrogen atom by methyl in the methyl or ethyl derivatives of these acids, a rise of 2° in the boiling point takes place in the even carbon atom series, whilst in the odd members a fall of 2° is effected. The melting points of the amides of the even terms form a descending series, whilst with the odd members the reverse is the case. The specific gravities of the methyl and ethyl derivatives diminish with an increase in molecular weight in both the odd and even series.

T. H. P.

Synthesis of Parabanic Acid. By PAUL CAZENEUVE (*Compt. rend.*, 1899, 129, 834-836).—Parabanic acid is obtained in small quantity by boiling oxamide with phenyl carbonate, and can be identified by its physical properties, and by conversion into calcium oxalurate, and by other chemical reactions.

C. H. B.

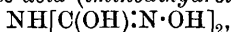
Constitution and Synthetical Application of Mercury Fulminate. I. Direct Aldoximation of Benzene. By ROLAND SCHOLL (*Ber.*, 1899, 32, 3492-3501).—Mercury fulminate moistened with benzene (100 grams) is mixed with benzene (150 grams) in a conical flask of $\frac{1}{2}$ litre capacity, provided with a delivery tube and a thermometer, which dips into the liquid. Aluminium hydroxide dried for 3 hours at about 130° (15 grams), commercial crystallised aluminium chloride, $AlCl_3 + 6H_2O$ (15 grams), and freshly prepared, sublimed aluminium chloride (120 grams) are pounded together for $\frac{1}{4}$ hour in a mortar provided with an india-rubber cap, through which the pestle passes. The mixture in the flask is heated to 45° in a water-bath, and then the aluminium chloride mixture is introduced in portions of 5-10 grams in the course of about 40 minutes, the flask being well shaken all the time. The thermometer is watched and the temperature kept at $43-45^\circ$ meanwhile, and also for $\frac{1}{2}-\frac{3}{4}$ hour longer, until it begins to fall of itself. The mixture is allowed to remain for at least 3 hours at the ordinary temperature, pounded in a mortar with crushed ice (700 grams) and concentrated hydrochloric acid (50 c.c.), and extracted with large volumes of ether. The ether is distilled off; mercuric chloride is removed by extracting several times with saturated sodium chloride solution, the benzaldoxime is removed by extraction with 25 per cent. caustic potash, benzaldehyde

with 40 per cent. sodium hydrogen sulphite solution, and benzonitrile by distillation, with or without steam; benzamide remains. About 80 grams of the fulminate enter into the reaction, and the yield of benzaldoxime is about 70 per cent. of the theoretical.

The reaction $C_6H_6 + C:N \cdot OH = C_6H_5 \cdot CH:N \cdot OH$ is further evidence that fulminic acid is carbonyl oxime (compare Nef., Abstr., 1895, i, 10). The aldoxime is a primary product of the reaction, and so is the nitrile in a sense, resulting probably from the action on the benzene of cyanogen chloride formed from the fulminate; the aldehyde and amide are formed from these. The yield of aldoxime depends on the observance of the details; if pure aluminium chloride is used without admixture of hydroxide or hydrated chloride, the nitrile is the main product. Homologues of benzene and alkoxybenzenes react in the same way as benzene, *m*-dihydroxybenzene derivatives yield aldoximes with the fulminate and hydrogen chloride, without addition of aluminium chloride; presumably monochloroformaldoxime is first formed.

C. F. B.

Action of Nitric Peroxide on Mercurydimethyl. By EUGEN BAMBERGER AND JENS MÜLLER (*Ber.*, 1899, 32, 3546—3554.)—The *oxime of iminodicarboxylic acid (iminodihydroxamic acid)*,



is obtained when a perfectly dry ethereal solution of nitric peroxide is slowly added to an ethereal solution of mercurydimethyl, cooled by the aid of a freezing mixture, and kept in constant agitation; it separates as large, colourless needles, which are extremely unstable, and can only be analysed with the greatest difficulty. It dissolves readily in water, yielding an acid solution, but is practically insoluble in ether. It decomposes when warmed by the finger, and explodes violently when dissolved in hydrochloric acid containing a little potassium chlorate in solution. Alkalis dissolve it, yielding a yellow solution smelling slightly of diazomethane, which when acidified and then shaken with ether, imparts a deep blue colour to the ethereal layer; when the ether is evaporated, a colourless, crystalline substance is obtained which possesses the properties of a pseudonitrole, but which has not been further investigated. Mineral acids decompose iminodihydroxamic acid, yielding formic acid, nitrous oxide, hydroxylamine, carbon monoxide and dioxide, ammonia, and probably nitrogen.

An ethereal solution of nitric peroxide reacts with an ethereal solution of formoxime in one of two ways, yielding either clear, glistening plates, which decompose at about 80°, or *formoxime nitrate*,



which crystallises in compact prisms melting at about 120°. The compound decomposing at 80° may be identical with the pseudonitrole derivative mentioned above.

J. J. S.

Heat of Neutralisation and Acidimetry of Cacodylic Acid. By HENRI IMBERT (*Compt. rend.*, 1899, 129, 1244—1246)—Cacodylic acid, when dissolved in water, is neutral towards methyl-orange, but towards phenolphthalein it behaves as a monobasic acid. Its heat of neutralisation is 14.10 cals., this value corresponding with the results obtained by Belugou for the action of caustic soda on the acid salts of

the monoalkylphosphates; these compounds, like cacodylic acid, are also neutral to methyl-orange and monobasic to phenolphthalein.

G. T. M.

Cyclic Polymethylenes of [Russian] Petroleum. By RUDOLF WISCHIN (*Chem. Zeit.*, 1899, 23, 916—926).—A summary and bibliography of the present state of knowledge of the composition of Russian petroleum, and of the naphthenes, naphthylenes, terpenes, and acids of the naphthene series, which either occur in it or have been prepared synthetically.

G. T. M.

New Compounds of Phosphoric Oxide with Benzene. By H. GIRAN (*Compt. rend.*, 1899, 129, 964—966. Compare Abstr., 1898, i, 407).—Further examination of the brick-red product obtained (*loc. cit.*) by heating together benzene and phosphoric oxide at 110—120° shows it to be *benzenemonodimetaphosphoric acid*, $C_6H_5 \cdot P_2O_4 \cdot OH$; it is very deliquescent, and is acted on by water with the production of benzene and phosphoric acid. It forms a deep yellow, deliquescent ammonium salt, $P_2O_5PhNH_4$, which is decomposed by water, yielding ammonium phosphate and benzene; the sodium and potassium salts form yellow precipitates rapidly decomposed by water.

At higher temperatures (200—210°), benzene and phosphoric anhydride combine to form *benzenetridimetaphosphoric acid*, $C_6H_5 \cdot 3P_2O_5 = C_6H_5(P_2O_4 \cdot OH)_3$, which is a yellow, deliquescent substance slightly soluble in alcohol, insoluble in benzene, ether, carbon disulphide, or chloroform, and is decomposed by water. The ammonium salt, $C_6H_5(P_2O_5NH_4)_3$, is a light yellow substance.

T. H. P.

Constitution of α -Dibromodinitrobenzene. By D. F. CALHANE and P. M. WHEELER (*Amer. Chem. J.*, 1899, 22, 449—458).—Austen's " α -dibromodinitrobenzene" (Abstr., 1876, ii, 406), on reduction with zinc dust and acetic acid, yields 3:6-dibromo-o-phenylenediamine, which, on distillation with steam, is obtained in felted, slender, white needles melting at 94—95°; it cannot be crystallised from hot water, as it is thereby partially decomposed. The hydrochloride forms white, lustrous needles, and is decomposed on heating, either alone or with water; the diacetyl derivative, $C_6H_2Br_2(NHAc)_2$, crystallises from hot alcohol in white, thread-like, matted crystals, and melts and decomposes at 265—269°. The base is converted by further reduction with sodium amalgam into o-phenylenediamine, and condenses with phenanthraquinone to form p-dibromophenanthraphenazine or phenanthra-p-dibromophenoquinoxaline, $C_{20}H_{10}N_2Br_2$, which crystallises from benzene in concentric aggregates of silky, yellow needles; with benzil, 5:8-dibromo-2:3-diphenylquinoxaline, $C_{20}H_{12}N_2Br_2$, crystallising in sheaf-like aggregates of needles and melting at 215—216°, is obtained.

These facts show that Austen's dinitro-compound is 1:4-dibromo-2:3-dinitrobenzene.

W. A. D.

Rate of Substitution of a Nitro-group by an Alkoxy. By CORNELIS A. LOBRY DE BRUYN (*Proc. K. Akad. Wetensch. Amsterdam*, 1898, 1, 144—148. Compare Abstr., 1899, i, 744—747).—A discussion of results already published.

G. T. M.

Phenyl- and *p*-Chlorophenyl-nitromethane. By A. VAN RAALTE (*Rec. Trav. Chim.*, 1899, 18, 378—407).—The boiling point curve of mixtures of *p*-chlorotoluene and *p*-chlorobenzyl chloride rises continuously between 158° and 215°; so that, in preparing *p*-chlorobenzyl chloride by the action of chlorine on boiling *p*-chlorotoluene, the reaction is complete when the temperature of the boiling liquid reaches 215°.

p-Chlorobenzyl iodide, $C_6H_4Cl \cdot CH_2I$, prepared by the action of potassium iodide on the corresponding chloride, is soluble in ether or alcohol, and crystallises from the latter in colourless needles melting at 64°, which smell something like aniseed, and strongly attack the mucous membranes of the eyes and nose. By acting on the iodide with silver nitrite, *p*-chlorophenylnitromethane [*p*-chloro-*o*-nitrotoluene], $C_6H_4Cl \cdot CH_2 \cdot NO_2$, is obtained; this compound exists in two modifications, the normal form melting at 33—34°. The *iso*-compound, $C_6H_4Cl \cdot CH \cdot NO \cdot OH$, which melts at 64°, gradually changes into the normal form, the melting point passing through a minimum of about 28°. In phenol solution, both modifications give the normal depression of freezing point; in acetic acid, the *iso*-compound has the normal molecular weight, whilst in diphenylmethane the mean value obtained is 208.5 instead of 171.5. The normal modification acts like a pseudo-acid, dissolving only slowly in caustic alkali solution; further, it gives no reaction with ferric chloride, forms a neutral aqueous solution, and a *N*/50 solution in a mixture of equal parts of methyl alcohol and water is a bad conductor of electricity. The *iso*-compound, on the other hand, acts as an acid, as it dissolves readily in sodium carbonate solution, gives a deep coloration with ferric chloride, and forms an acid aqueous solution; it also has a high conductivity which, however, falls as the *iso*-form becomes converted into the normal compound.

Acetylbenzhydroxamic acid, $COPh \cdot NH \cdot OAc$, obtained by the action of acetyl chloride on either sodium phenylnitromethane or benzhydroxamic acid, forms small, white needles melting at 125—126°.

p-Chlorobenzoylbenzhydroxamic acid, $COPh \cdot NH \cdot O \cdot CO \cdot C_6H_4Cl$, prepared by the action of *p*-chlorobenzoyl chloride on benzhydroxamic acid, separates from benzene in colourless crystals melting at 137°.

p-Chlorobenzhydroxamic acid, $C_6H_4Cl \cdot CO \cdot NH \cdot OH$, crystallises in small, shining plates melting at 168°, and *p*-dichlorodibenzhydroxamic acid, $C_6H_4Cl \cdot CO \cdot NH \cdot O \cdot CO \cdot C_6H_4Cl$, when crystallised from acetic acid, melts at 165°.

Benzoyl-p-chlorobenzhydroxamic acid, $C_6H_4Cl \cdot CO \cdot NH \cdot O \cdot Bz$, when deposited from benzene solution, melts at 158°. T. H. P.

Separation of Primary, Secondary, and Tertiary Amines by Ginsberg's Method. By WASSILY SOLONINA (*Chem. Centr.*, 1899, ii, 867—868; from *J. Russ. Chem. Soc.*, 1899, 31, 640—655. Compare *ibid.*, 29, 404).—The investigation of the action of benzenesulphonic chloride, and in some cases of *p*-bromobenzenesulphonic chloride and *m*-nitrobenzenesulphonic chloride on eleven primary amines of the fatty, and on five of the aromatic series, shows that Ginsberg's method of separating primary and secondary amines, which depends

on the different solubility of the products of these reactions, is in many cases inapplicable.

Of the following compounds, those of the type $\text{NHR} \cdot \text{SO}_2\text{Ph}$ are soluble in alkalis, except where it is stated to the contrary, whilst those of the type $\text{NR}(\text{SO}_2\text{Ph})_2$ are insoluble; the compounds of both classes are usually easily soluble in hot alcohol, ether, or benzene.

By the action of benzenesulphonic chloride on butylamine in presence of potassium hydroxide, *benzenesulphonbutylamide*, $\text{C}_4\text{H}_9 \cdot \text{NH} \cdot \text{SO}_2\text{Ph}$, and *dibenzenesulphonbutylamide*, $\text{C}_4\text{H}_9 \cdot \text{N}(\text{SO}_2\text{Ph})_2$, are formed. The former is an oil which is insoluble in water, and when treated with nitric acid of sp. gr. 1.48 forms *benzenesulphonbutylnitramide*, $\text{C}_4\text{H}_9 \cdot \text{N}(\text{NO}_2) \cdot \text{SO}_2\text{Ph}$, which crystallises in colourless plates, melts at 29° , is insoluble in water or alkalis, but easily soluble in alcohol, ether, or benzene. *Dibenzenesulphonbutylamide* crystallises in plates, melts at $89-90^\circ$, and is insoluble in water and slightly soluble in cold alcohol. *p-Bromobenzenesulphonbutylamide* melts at 58° and yields a *nitramide* which melts at $37-38^\circ$. *Di-p-bromobenzenesulphonbutylamide* melts at 116° and is slightly soluble in cold alcohol. *m-Nitrobenzenesulphonbutylamide* is crystalline, melts at $69-70^\circ$, and by the action of nitric acid yields the *nitramide*, which is crystalline, melts at $80-81^\circ$, and is insoluble in water or alkalis. *Di-m-nitrobenzenesulphonbutylamide* is crystalline, melts at 136° , and is insoluble in water. By the action of benzenesulphonic chloride on propylamine, *benzenesulphonpropylamide*, $\text{NHPr} \cdot \text{SO}_2\text{Ph}$, is formed, together with a small quantity of a compound which melts at 65° , is insoluble in alkalis, and probably consists of *dibenzenesulphonpropylamide*. The former forms white crystals, melts at 36° , and by the action of nitric acid yields the *nitramide*, which melts at $34-35^\circ$. When *p-bromobenzenesulphonic chloride* acts on propylamine, *di-p-bromobenzenesulphonpropylamide*, melting at 27° , is formed in small quantity together with *p-bromobenzenesulphonpropylamide*, which forms white crystals, melts at 65° , is insoluble in water, and by the action of nitric acid yields the *propylnitramide*, which melts at 44° . *Dibenzenesulphonmethylethylamide*, $\text{NMe}(\text{SO}_2\text{Ph})_2$, melts at $104-105^\circ$. Ethylamine under similar conditions forms only *benzenesulphonethylethylamide*. *p-Bromobenzenesulphonethylethylamide* melts at 81° , the *di-p-bromobenzenesulphonethylethylamide* at 132° . By the action of benzenesulphonic chloride on β -aminobutane, *benzenesulphonpseudobutylamide*, melting at 70.5° , is alone formed. *p-Bromobenzenesulphonpseudobutylamide* melts at 80° . *m-Nitrobenzenesulphonpseudobutylamide*, $\text{C}_4\text{H}_9 \cdot \text{NH} \cdot \text{SO}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{NO}_2$, melts at 58° . *Benzenesulphonisopropylamide* melts at 26° , and *p-bromobenzenesulphonisopropylamide* at 99.5° . The corresponding *nitramides* melt at 35° and $82-83^\circ$. *Benzenesulphonvalerylamine*, prepared from β -aminopentane, is insoluble in water and melts at 40° . ϵ -Amino- α -hexylene forms only *benzenesulphonhexylamide* melting at $36.5-37^\circ$. *Benzenesulphonallylamine*, prepared from allylamine, melts at $39-40^\circ$.

By the action of benzenesulphonic chloride on aniline and *m*-xylylidine, compounds of the type $\text{NHR} \cdot \text{SO}_2\text{Ph}$ soluble in alkalis are formed. When an excess of the acid chloride is used, or by the action of the chloride on the preceding compounds in presence of alkali, small

quantities of the compounds $\text{NR}(\text{SO}_2\text{Ph})_2$ are produced. *Dibenzenesulphonanilide*, $\text{NPh}(\text{SO}_2\text{Ph})_2$, forms white crystals and melts at $128-129^\circ$. The *benzoyl* derivative, $\text{NPhBz}\cdot\text{SO}_2\text{Ph}$, crystallises in needles and melts at $112-113^\circ$. *Benzenesulphon-m-xylide* forms prismatic crystals and melts at $130-131^\circ$. *Dibenzenesulphon-m-xylide*, $\text{C}_6\text{H}_3\text{Me}_2\cdot\text{N}(\text{SO}_2\text{Ph})_2$, crystallises in small needles and melts at 142° .

Benzenesulphonheptylamide, $\text{C}_7\text{H}_{15}\cdot\text{NH}\cdot\text{SO}_2\text{Ph}$, differs from the preceding compounds of the same type in being insoluble in alkalis. *Dibenzenesulphonheptylamide* forms leaf-like crystals, melts at 91° , and is insoluble in alkalis. α -Camphylamine yields *benzenesulphon- α -camphylamide*, which is a viscous oil and is also insoluble in alkalis. *Dibenzylsulphoncamphylamide*, $\text{C}_{10}\text{H}_{17}(\text{SO}_2\text{Ph})_2$, is also formed, but could not be isolated. *p*-Bromobenzenesulphonic chloride and *m*-nitrobenzenesulphonic chloride react in a similar manner to benzenesulphonic chloride. *Benzenesulphonisoundecylamide*, prepared from β -aminoundecane, melts at $64-65^\circ$ and is insoluble in alkalis, but soluble in alcohol, ether, or benzene. Aminomenthone yields a sulphobenzene derivative, $\text{C}_{10}\text{H}_{17}\text{O}\cdot\text{NH}\cdot\text{SO}_2\text{Ph}$, which melts at $82-85^\circ$ and is soluble in alkalis. No definite compounds could be isolated from the products of the action of benzenesulphonic chloride on diamino-hexahydrocymene. Details of a crystallographic examination of dibenzenesulphonbenzylamide are given in the original paper. E. W. W.

Behaviour of Sulphonamides of Primary Amines towards Alkalis. By WILHELM MARCKWALD (*Ber.*, 1899, 32, 3512—3513. Compare *Abstr.*, 1899, i, 749, and Solonina, preceding abstract).—Benzenesulphonheptylamide does not dissolve in dilute sodium hydroxide (compare Solonina), but is nevertheless partly converted into the sparingly soluble sodium salt, which solidifies when shaken with strong sodium hydroxide, and can be recrystallised from acetone. Hinsberg's rule therefore holds good, but, as in other cases, the salt is partially hydrolysed by water. T. M. L.

Fixation of Sodium Hydrogen Sulphite by Ethylene Linkings. By HENRI LABBÉ (*Bull. Soc. Chim.*, 1899, [iii], 21, 1077—1080).—It would appear from Tiemann's researches on aldehydes and ketones that the fixation of sodium hydrogen sulphite by an ethylene linking generally should depend largely on the characteristic function of the molecule, and a series of experiments was made with various typical substances in order to ascertain whether this was the case. When styrene is boiled for 10 hours in a reflux apparatus with excess of sodium hydrogen sulphite solution, only traces of an organic salt are formed, but cinnamyl alcohol under the same conditions yields a notable quantity of a white, deliquescent, very soluble salt of the composition $\text{C}_9\text{H}_{11}\text{O}_4\text{SNa}$. Geraniol and citronellol form similar compounds of the composition $\text{C}_{10}\text{H}_{20}\text{O}_4\text{S}_2\text{Na}_2$ and $\text{C}_{10}\text{H}_{21}\text{O}_4\text{SNa}$ respectively; in the case of geraniol, the yield is about 15 per cent. With cinnamic acid, the reaction occurs much more readily, a large yield of the compound $\text{C}_9\text{H}_8\text{O}_6\text{SNa}_2$ being obtained; this salt is, however, difficult to separate on account of its very sparing solubility in

alcohol. It is concluded that the fixation of sodium hydrogen sulphite by an ethylene linking takes place with great difficulty in the case of aromatic hydrocarbons with an aliphatic side-chain, but more readily in the case of alcohols, especially aliphatic alcohols of the type of geraniol, whilst with acids, probably because of their solubility, combination occurs with great ease.

N. L.

Resin Oil. By GUSTAV KRAEMER and ADOLF SPILKER (*Ber.*, 1899, 32, 3614).—The oil obtained by distilling colophony under pressure (*Ber.* 1899, 32, 2952), to which the authors assigned the formula $C_{42}H_{62}$, appears, from a determination of its molecular weight by the cryoscopic method, to have the composition $C_{18}H_{28}$, and is perhaps derived from abietic acid by the loss of 1 mol. of carbon dioxide.

W. A. D.

Conversion of 1:8- and 1:5-Dinitronaphthalenes into Nitronitrosonaphthols. By PAUL FRIEDLÄNDER (*Ber.*, 1899, 32, 3528—3532. Compare Graebe, this vol., i, 24).—If the action of sulphuric acid on dinitronaphthalene is continued until the product is completely soluble in alkali, sulphonation occurs; the sulphonic acids are converted on nitration into trinitronaphthols identical with those produced on nitrating the nitronitrosonaphthol, which forms the chief product of the action, and are therefore 8- or 5-nitro-4-nitroso-1-naphthol-3-sulphonic acids. 8-Nitro-4-nitroso-1-naphthol gives a *benzoate* which crystallises from xylene in yellowish-white, slightly soluble needles and melts at 194° , whilst the 5:4-derivative gives a similar *benzoate* which melts at 210° . The nitronitrosonaphthols are converted by alkaline potassium ferricyanide into the potassium salts of the corresponding dinitronaphthols; 4:5-dinitro-1-naphthol crystallises in straw-yellow needles and melts at 230° , whilst 4:8-dinitro-1-naphthol melts at 135° ; the dinitronaphthols have only feeble dyeing properties but give trinitronaphthols which resemble naphthol yellow in this respect.

4:8-Diamino-1-naphthol is oxidised by cold ferric chloride to a blue solution of the quinoneimide, but, on warming, to a red solution of 5-amino- α -naphthaquinone, which crystallises from acetic acid, melts and decomposes at about 180° , and dissolves in sulphuric acid to a colourless, crystalline salt.

1:3-Dinitronaphthalene is not produced in the nitration of nitronaphthalene by nitrosulphuric acid; the 1:5- and 1:8-dinitronaphthols can be very readily separated by crystallising from pyridine instead of extracting with acetone; by using suitable quantities of sulphuric acid in the nitration, a similar separation can be effected, the whole of the 1:5-dinitronaphthalene crystallising out on cooling, whilst the 1:8-dinitronaphthalene remains in solution, and can be converted directly, if desired, into 1:3:8-trinitronaphthalene by adding a further amount of nitric acid.

1:3:8-Trinitronaphthalene dissolves in cold sodium hydrogen sulphite to a red solution of an additive compound, from which it is precipitated unchanged by warming with acids,

T. M. L.

Fittig's Reaction. By MICHEL PELLEGRIN (*Rec. Trav. Chim.*, 1899, 18, 457—465).—By the action of sodium on a mixture of *m*-xylylene dibromide and bromobenzene, three definite products were obtained. 1. Diphenyl. 2. *m*-Dixylylene (?), $C_{16}H_{16}$, slightly soluble in alcohol or ether and crystallising from the latter in hexagonal prisms melting at 131.5° ; cryoscopic determinations in benzene gave a mean molecular weight 205.5, $C_{16}H_{16}$ requiring the number 208. It boils at 170° under 12 mm. and at 290° under the ordinary pressure, and forms a dibromo-derivative, $C_{16}H_{14}Br_2$, crystallising from benzene in colourless prisms which melt at 213 — 214° . 3. *Di-m-phenylene-diethene* (?), $C_6H_4 \begin{smallmatrix} \text{CH:CH} \\ \text{CH:CH} \end{smallmatrix} C_6H_4$, which crystallises from a mixture of ether and alcohol in long, silky, colourless needles, melts at 191° , boils at 260° under 12 mm. pressure, and is very soluble in ether, but less so in alcohol, benzene, or carbon disulphide. In freezing benzene, it has the mean molecular weight 200.9, the value for $C_{16}H_{12}$ being 204.

The only definite product obtained by the action of sodium on a mixture of *m*-bromobenzene and benzyl chloride was dibenzyl.

T. H. P.

Synthesis of Picene. By T. HIRN (*Ber.*, 1899, 32, 3341—3343. Compare Abstr., 1892, 623, and 1895, i, 292).—Picene is a phenanthrene of the naphthalene series and contains a linking joining the two naphthalene residues in the $\beta\beta'$ -position. The exact position of the dimethenyl group is, however, not known with certainty, and accordingly three formulæ for picene are possible; it may be an $\alpha\beta\alpha'\beta'$ -, a $\beta\beta\beta'\beta'$ - or an $\alpha\beta\beta'\beta'$ -derivative. The first of these constitutions is the most probable, because the hydrocarbon is produced when $\alpha\alpha'$ -dinaphthastilbene (Abstr., 1893, 272) is distilled through a red hot glass tube. The properties of the product correspond with those of picene from coal-tar, except that the xylene solution of the former is not fluorescent.

G. T. M.

Double Halogen Salts of Tin with Organic Bases. By GEORGE M. RICHARDSON and MAXWELL ADAMS (*Amer. Chem. J.*, 1899, 22, 446—449).—In addition to the compounds obtained by Slagle (Abstr., 1899, i, 39), the following have been prepared. *Tetraniline stannichloride*, $(NH_2Ph)_4 \cdot 4HCl \cdot SnCl_4$, is obtained in well-formed crystals. *Dimethylaniline stannochloride*, $NMe_2Ph \cdot HCl \cdot SnCl_2 + \frac{1}{2}H_2O$, corresponds in preparation and crystalline form with Slagle's analogous toluidine compounds.

Aniline stannobromide, $NH_2Ph \cdot HBr \cdot SnBr_2$, forms small, white, spear-like crystals, which melt at 152° , and become oxidised on being recrystallised. *Dianiline stannibromide*, $(NH_2Ph)_2 \cdot H_2SnBr_6$, forms flat, tabular, straw-coloured crystals, whilst *tetraniline stannibromide*, $(NH_2Ph)_4 \cdot 4HBr \cdot SnBr_4$, which is less soluble in water than the dianiline compound, separates in light-yellow, well-formed crystals, and melts and decomposes at 274° .

W. A. D.

Anilides. By FREDERICK D. CHATTAWAY, KENNEDY J. P. ORTON, and W. H. HURTLEY (*Ber.*, 1899, 32, 3635—3638. Compare Trans., 1899, 75, 1046, and following abstract).—The following anilides have

been obtained by the transformation of substituted nitrogen chlorides or bromides.

p-Chloroformylanilide, obtained from the isomeric phenylformyl-nitrogen chloride, crystallises in white plates and melts at 102°.

2 : 4-Dichloroformylanilide, prepared either from the corresponding nitrogen chloride or by formylating 2 : 4-dichloroaniline, crystallises from alcohol in white needles melting at 154°; the benzoyl derivative forms white prisms and melts at 115°.

2 : 4 : 6-Trichloroformylanilide crystallises from alcohol or chloroform in white needles and melts at 180°; the acetyl derivative is most conveniently prepared from acetyl-2 : 4-dichlorophenyl nitrogen chloride; the benzoyl derivative crystallises from alcohol in white needles melting at 174°.

2 : 4-Dibromoformylanilide forms lustrous, white needles melting at 145°; the acetyl derivative is readily prepared from the isomeric acetyl-*p*-bromophenyl nitrogen bromide.

2 : 4 : 6-Tribromoformylanilide, crystallises in white needles and melts at 221.5°; the acetyl derivative is easily obtained from acetyl-2 : 4-dibromophenyl nitrogen bromide.

1-Chloro-2-formylnaphthalide crystallises from benzene in prisms melting at 136°.

G. T. M.

Substituted Nitrogen Bromides and their Relationship to Bromo-substituted Anilides and Anilines. By FREDERICK D. CHATTAWAY and KENNEDY J. P. ORTON (*Ber.*, 1899, 32, 3573—3582. Compare *Trans.*, 1899, 75, 1046).—Substituted nitrogen bromides of the type $R \cdot CO \cdot NBrR'$ are readily obtained by the action of hypobromous acid on the corresponding anilides. They are all sulphur-yellow compounds of low melting point, crystallising from light petroleum either in large, transparent prisms or in plates, and are characterised by the readiness with which they enter into various chemical reactions. They react with hydrobromic acid, hydrocyanic acid, potassium iodide solution, or hydrogen peroxide, regenerating the original anilide. They are much more easily hydrolysed than the corresponding chlorides (*loc. cit.*), and are readily decomposed by alcohol, yielding the anilide, together with ethyl bromide, acetaldehyde, and ethyl acetate. When heated, all these nitrogen bromide derivatives undergo molecular transformation, the bromine atom migrating from the nitrogen to a carbon atom of the benzene nucleus, always in the para-position unless this is already occupied, when an ortho-derivative is formed. The authors conclude that in the ordinary bromination of an aniline or anilide the bromine becomes first attached to the nitrogen atom and then passes to the benzene nucleus.

Acetylphenyl nitrogen bromide (*N*-bromoacetylanilide, *acetylphenyl bromamide*), $NPhBrAc$, obtained by the action of hypobromous acid on a cold saturated solution of acetylanilide at 0° containing potassium hydrogen carbonate, melts at 88°, is readily soluble in chloroform, but only moderately so in light petroleum; when kept for any length of time, it gradually becomes transformed into *p*-bromoacetylanilide.

Acetyl-p-bromophenyl nitrogen bromide, $C_6H_4Br \cdot NBrAc$, crystallises in

six-sided plates melting at 108° ; the isomerisation is not complete even after the bromide has been kept for some months. The 2:4-*dibromo*-derivative melts at 110° , and is quite stable at the ordinary temperature. The 2:4:6-*tribromo*-derivative melts at 123° , and when strongly heated gives up bromine and forms 2:4:6-tribromoacetylanilide. *Formylphenylnitrogen bromide*, $\text{NPhBr}\cdot\text{CHO}$, melts at $88-89^{\circ}$, and when allowed to remain for 24 hours is completely transformed into *p*-bromoformylanilide. The *p*-*bromo*-derivative melts at 113° ; the 2:4-*dibromo*-derivative melts at 87° and the 2:4:6-*tribromo*-derivative at 90° . *Benzoylphenylnitrogen bromide* (*N*-*bromobenzoylanilide*, *benzoylphenylbromamide*), NBrPhBz , is best obtained by allowing an alcoholic solution of benzoylanilide to drop slowly into an excess of hypobromous acid containing potassium hydrogen carbonate in solution at 0° ; it crystallises in small, yellow plates melting at 99° , and is readily transformed into benzoyl-*p*-bromophenylnilide. The *p*-*bromo*-derivative melts at $132-133^{\circ}$; the 2:4-*dibromo*-derivative melts and decomposes at 121° , and when heated for half an hour at 100° yields 2:4:6-tribromobenzoylanilide melting at 198° . The 2:4:6-*tribromo*-derivative melts at 121° . J. J. S.

Symmetrical Dinitrodixylylcarbamides and Dinaphthylcarb-amides. By HENRI VITTENET (*Bull. Soc. Chim.*, 1899, [iii], 21, 948-951).—These compounds have been prepared by methods similar to those employed for the preparation of the dinitrodiphenylcarb-amides and the dinitroditylcarb-amides (Abstr., 1899, i, 692, 810), namely, by heating the isomeric nitroxylidines and naphthylamines with carbonyl chloride or phenyl carbonate.

Dinitrodixylylcarbamide, $\text{CO}(\text{NH}\cdot\text{C}_6\text{H}_2\text{Me}_2\cdot\text{NO}_2)_2$ [$\text{NH}:\text{Me}_2:\text{NO}_2=4:1:3:5$], from 5-nitro-1:3:4-*m*-xylylidine, crystallises from anhydrous acetic acid in small, yellow needles, subliming without melting at about 300° , and is insoluble in water, benzene, ether, or chloroform. Like other compounds in which the NO_2 and NH_2 groups occupy the ortho-position with regard to each other, 5-nitro-1:3:4-*m*-xylylidine reacts with carbonyl chloride, but not with phenyl carbonate.

Dinitrodixylylcarbamide [$\text{NH}:\text{Me}_2:\text{NO}_2=4:1:3:6$] is only obtained in very small quantity by the general methods indicated above, and is best prepared by the action of 6-nitro-1:3:4-*m*-xylylidine on 6-nitro-1:3:4-*m*-xylylcarbimide in benzene solution. It crystallises in microscopic, white needles which sublime without melting when heated, and is insoluble in water, benzene, ether, and chloroform.

α - and β -*Dinaphthylcarb-amides*, prepared by this method, were found to melt at $314-315^{\circ}$ and $309-310^{\circ}$ respectively, not at 270° and 293° as previously stated.

[Young and Clark (*Trans.*, 1897, 71, 1200, give the melting points at $284-286^{\circ}$ and $289-290^{\circ}$.) N. L.]

Aromatic Carbimides. By HENRI VITTENET (*Bull. Soc. Chim.*, 1899, [iii], 21, 952-958).—The following new compounds have been obtained by the action of carbonyl chloride on aromatic bases, according to the general method which has been recently described (Abstr., 1899, i, 756).

5-Nitro-*m*-xylylcarbimide, $\text{NO}_2 \cdot \text{C}_6\text{H}_2\text{Me}_2 \cdot \text{N} : \text{CO}$ [$\text{Me}_2 : \text{N} : \text{CO} : \text{NO}_2 = 1 : 3 : 4 : 5$], from 5-nitro-1 : 3 : 4-*m*-xylidine, crystallises in microscopic, yellow needles melting at $71-72^\circ$ and is soluble in benzene, toluene, ether, chloroform, or light petroleum.

Ethyl 5-nitro-*m*-xylylcarbamate [$\text{Me}_2 : \text{NH} \cdot \text{CO}_2\text{Et} : \text{NO}_2 = 1 : 3 : 4 : 5$] formed by the interaction of alcohol and the preceding compound, crystallises from 95 per cent. alcohol in small, amber-yellow prisms melting at $125-126^\circ$; it is soluble in chloroform.

6-Nitro-1 : 3 : 4-*m*-xylylcarbimide, from 6-nitro-1 : 3 : 4-*m*-xylidine, crystallises in large, yellow needles melting at a few degrees above zero and distilling without decomposition at $212-214^\circ$ under 97 mm. pressure.

Ethyl 6-nitro-1 : 3 : 4-*m*-xylylcarbamate, obtained by the action of alcohol on the preceding compound, crystallises from alcohol in large, white needles melting at 120° ; it is insoluble in cold, but soluble in boiling water.

p-Chlorophenylcarbimide, from *p*-chloroaniline and carbonyl chloride, is a white, crystalline substance which melts at $30-31^\circ$ to a colourless liquid having a very irritating odour.

Ethyl *p*-chlorophenylcarbamate, prepared by treating the corresponding carbimide with alcohol, crystallises in white, silky plates melting at 68° , and is very soluble in ether, benzene, or chloroform.

m-Chlorophenylcarbimide, from *m*-chloroaniline, is a colourless liquid of irritating odour which boils at $113-114^\circ$ under 43 mm. pressure.

Ethyl *m*-chlorophenylcarbamate, from the corresponding carbimide and alcohol, is an unstable, viscous, colourless liquid which boils at $200-201^\circ$ under 46.5 mm. pressure.

o-Chlorophenylcarbimide, from *o*-chloroaniline, is a colourless liquid boiling at $114-115^\circ$ under 43 mm. pressure and having a very irritating odour.

Ethyl *o*-chlorophenylcarbamate, from the preceding compound and alcohol, is a colourless liquid which boils at $170-172^\circ$ under 42 mm. pressure.

p-Iodophenylcarbimide, from *p*-iodoaniline, is a crystalline substance of agreeable odour melting at $45-46^\circ$; it is very unstable and quickly decomposes, yielding the corresponding carbamide.

Ethyl *p*-iodophenylcarbamate crystallises in large, white needles melting at $111-112^\circ$ and is very soluble in ether, benzene, or chloroform.

p-Methoxyphenylcarbimide, from *p*-anisidine, is a colourless liquid which quickly becomes yellow and decomposes; it boils at $132-133^\circ$ under 38.5 mm. pressure.

Ethyl *p*-methoxyphenylcarbamate crystallises in large, white needles melting at $63-64^\circ$; it is very soluble in ether, chloroform, or benzene.

α -Naphthylcarbamide, from α -naphthylamine, is a brown liquid having a very irritating odour. Ethyl α -naphthylcarbamate crystallises in small, white needles melting at 79° . This and the preceding compound have been previously obtained by Hofmann by other methods.

β -Naphthylcarbimide, from β -naphthylamine, crystallises from light

petroleum in white plates melting at 55—56° and is very soluble in ether or benzene.

Ethyl β-naphthylcarbamate, obtained by the action of alcohol on the corresponding carbimide crystallises from 40 per cent. alcohol in small, white needles melting at 69°; it is very soluble in ether, benzene, chloroform, or 95 per cent. alcohol. N. L.

Characteristics of Stereoisomeric Ammonium Salts. By EDGAR WEDEKIND (*Ber.*, 1899, 32, 3561—3569. Compare Abstr., 1899, i, 351, and Pope and Peachey, *Trans.*, 1899, 75, 1127).—*α*- (or *γ*)-*Phenylbenzylmethylallylammonium bromide* is obtained by the direct combination of benzylmethylaniline and allyl bromide or more readily of methylallylaniline and benzyl bromide; it melts and decomposes not very sharply at 161—163°, and dissolves readily in warm alcohol or water, but when its aqueous solution is boiled, decomposition ensues; it crystallises in the rhombic system and is isomorphous with the *α*-iodide (*loc. cit.*) [*a* : *b* : *c* = 0·88888 : 1 : 0·65854]. The *α*-chloride is obtained when the *α*-iodide is treated with moist silver oxide, then with concentrated hydrochloric acid, and the solution thus formed evaporated at 50—60°; it crystallises in large, spear-shaped, rhombic crystals isomorphous with the *α*-bromide and *α*-iodide, melts at 152—154°, and is readily soluble in most organic solvents with the exception of light petroleum and ether; it also dissolves in water, but the solution, when boiled, undergoes partial hydrolysis. The *platinichloride*, (C₁₇H₂₀N)₂PtCl₆, crystallises in minute, yellow needles and the *aurichloride* forms a yellow, amorphous powder melting at 90—94°.

β-*Phenylbenzylmethylallylammonium bromide* is obtained when benzylallylaniline and pure methyl bromide are left in contact with one another for several months at the ordinary winter temperature. It crystallises from a mixture of chloroform and acetone in well-developed, colourless, monoclinic plates, is specifically heavier and also melts at a lower temperature, namely, 105—107°, than the isomeric bromide. It is apparently hemihedral [*a* : *b* : *c* = 1·1128 : 1 : 1·3084; *β* = 71°45′]. The *β*-chloride, obtained indirectly from either the bromide or iodide, crystallises in small, glistening, monoclinic prisms isomorphous with the *β*-bromide [*a* : *b* : *c* = 1·054 : 1 : 1·260; *β* = 71°40′]. It decomposes at 113—116° whereas the *α*-chloride decomposes at 152—154°. The *β*-iodide (*loc. cit.*) is not isomorphous with the *β*-chloride and bromide; as it crystallises in the rhombic system; it may, however, be dimorphous. The *platinichloride* crystallises in brownish-yellow needles decomposing at 198—199°; the *β*-aurichloride forms golden-yellow needles melting at 105—107° and decomposing at about 180°. Both compounds are more soluble than the isomeric *α*-derivatives.

J. J. S.

Acyl Derivatives of the Aromatic Thiocarbamides: their Isomerism and Constitution. By A. HUGERSHOFF (*Ber.*, 1899, 32, 3649—3660).—Acyl derivatives of the aromatic thiocarbamides can be prepared by dissolving the carbamide in the acyl anhydride at about 80°, and allowing the solution to remain for some time at the ordinary temperature, whereas, if the solution is heated, decomposition occurs, and thiocarbimides are produced (*Werner, Trans.*, 1891, 59,

396). These compounds have not the properties of thiocarbamides, since they are soluble in alkalis, and are not desulphurised by mercuric oxide. They have probably the formula $\text{NR}:\text{C}(\text{SH})\cdot\text{NR}\cdot\text{COR}$, and this view is confirmed by the fact that the acyl derivatives of mono-substituted thiocarbamides exist in two forms, one of which behaves as a true thiocarbamide, whilst the more stable modification agrees in its properties with the ordinary acyl derivatives, which the author terms isothiocarbamides.

Acetyldiphenylisothiocarbamide, $\text{NPh}:\text{C}(\text{SH})\cdot\text{NPhAc}$, which has already been prepared by Deninger (Abstr., 1895, 461), melts at 96° , and not at 91° as stated by that author. Mercuric oxide converts it into the mercuric salt, $(\text{C}_{15}\text{H}_{13}\text{ON}_2\text{S})_2\text{Hg}$. Acetyldi-*o*-tolylisothiocarbamide, melts at 103° , whilst the corresponding *p*-tolyl compound melts at 108° . Acetyldiphenetylisothiocarbamide melts at 98° ; propionyldiphenylisothiocarbamide, $\text{NPh}:\text{C}(\text{SH})\cdot\text{NPh}\cdot\text{COEt}$, melts at 93.5° , whilst propionyldi-*o*-tolylisothiocarbamide melts at 97.5° , and the corresponding *p*-tolyl compound at 105° . Isovaleryldiphenylisothiocarbamide melts at 83° .

Acetylphenylthiocarbamide, $\text{NHPh}\cdot\text{CS}\cdot\text{NHAc}$, obtained by the action of acetic anhydride on phenylthiocarbamide, melts at 139° , but on further heating is converted into the iso-derivative melting at 171° . Concentrated aqueous alkalis decompose it, forming acetanilide and a thiocyanate, whilst dilute alkalis dissolve it, forming a solution from which acids precipitate the tautomeric form. It undergoes the usual reaction of a thiocarbamide with mercuric oxide, acetylphenylcarbamide being produced. The tautomeric form, $\text{NPh}:\text{C}(\text{SH})\cdot\text{NHAc}$, has already been described by Miquel (*Bull. Soc. Chim.*, 1875, [ii], 25, 252). Both the forms have the same molecular weight as determined by the cryoscopic method in acetic acid solution. Acetyl-*o*-tolylthiocarbamide, $\text{C}_6\text{H}_4\text{Me}\cdot\text{NH}\cdot\text{CS}\cdot\text{NHAc}$, melts at 140° and behaves in a similar manner to the phenyl derivative. The corresponding iso-derivative has been described (Dixon, *Trans.*, 1889, 55, 304). Acetyl-*p*-tolylthiocarbamide, melts at 137° . Acetylphenetylthiocarbamide melts at 137° , and the corresponding iso-derivative at 196° . A. H.

[Phenylthiocarbimide] as a Reagent for the Detection of the Alcoholic Hydroxyl Group. By WILLIAM R. ORNDORFF AND F. A. RICHMOND (*Amer. Chem. J.*, 1899, 22, 458—472).—Phenylthiocarbimide combines with aliphatic monohydroxy-alcohols to form well-defined thiourethanes, but does not interact in so simple a manner with unsaturated or polyhydroxy-alcohols, phenols, aromatic alcohols, or fatty or aromatic acids. In most cases, therefore, it cannot be used as a substitute for phenylcarbimide to detect the presence of a hydroxyl group.

Ethyl phenylthiocarbamate, $\text{NHPh}\cdot\text{CS}\cdot\text{OEt}$ or $\text{NPh}:\text{C}(\text{SH})\cdot\text{OEt}$, melts at 71 — 72° , not at 65° as stated by Hofmann (*Ber.*, 1869, 2, 120; 1870, 3, 772). Methyl phenylthiocarbamate, $\text{NHPh}\cdot\text{CS}\cdot\text{OMe}$, or $\text{NPh}:\text{C}(\text{SH})\cdot\text{OMe}$, prepared like the ethyl derivative, separates from alcohol in white, triclinic crystals [$a:b:c=0.6065:1:0.5513$; $\alpha=63^\circ19'57''$, $\beta=128^\circ52'50''$, $\gamma=103^\circ8'48''$], and melts at 97° . Propylphenylthiocarbamate, $\text{NHPh}\cdot\text{CS}\cdot\text{OPr}^a$ or $\text{NPh}:\text{C}(\text{SH})\cdot\text{OPr}^a$, prepared by

heating a mixture of propyl alcohol and phenylthiocarbimide for 16 hours at 100° , crystallises from absolute alcohol in white, triclinic needles and melts at 48° ; if a higher temperature than 100° is used in the preparation, gaseous products together with thiocarbanilide are formed. *Isopropyl phenylthiocarbamate*, $\text{NHPh}\cdot\text{CS}\cdot\text{OPr}^{\beta}$, or $\text{NPh}\cdot\text{C}(\text{SH})\cdot\text{OPr}^{\beta}$, prepared similarly, separates from alcohol in brilliant, colourless, monoclinic crystals, [$a : b : c = 0.6777 : 1 : 1.8325, \beta = 87^{\circ}28'50''$] and melts at 85.5° . The corresponding *isobutyl* compound,

$\text{NHPh}\cdot\text{CS}\cdot\text{O}\cdot\text{CH}_2\text{Pr}^{\beta}$ or $\text{NPh}\cdot\text{C}(\text{SH})\cdot\text{O}\cdot\text{CH}_2\text{Pr}^{\beta}$, crystallises from alcohol, and melts at 80.5° ; the *tertiary butyl* derivative, $\text{NHPh}\cdot\text{CS}\cdot\text{O}\cdot\text{CMe}_3$, or $\text{NPh}\cdot\text{C}(\text{SH})\cdot\text{O}\cdot\text{CMe}_3$, melts at the atmospheric temperature, but solidifies in a freezing mixture, forming long, white needles. *Isoamyl phenylthiocarbamate*, $\text{NHPh}\cdot\text{CS}\cdot\text{OC}_5\text{H}_{11}$, or $\text{NPh}\cdot\text{C}(\text{HS})\cdot\text{OC}_5\text{H}_{11}$, forms white crystals and melts at about 21° .

When allyl alcohol is heated with phenylthiocarbimide, symmetrical diphenylcarbamide is formed, but no thiourethane; in like manner, glycol and glycerol give rise only to diphenylthiocarbamide (compare Tessmer, *Abstr.*, 1885, 774), whilst in the case of glycol chlorohydrin, erythritol, or dextrose no action occurs. Phenol yields thiocarbanilide only, and not the corresponding thiourethane as stated by Dixon (*Trans.*, 1890, 57, 268), and Snape (*Trans.*, 1896, 69, 98); with quinol, pyrogallol, and benzyl alcohol there is no action.

On heating phenylthiocarbimide with acetic acid for 5 hours at 100° , symmetrical diphenylcarbamide is obtained; with benzoic acid under similar conditions, there is no action, whilst with lactic acid, thiocarbanilide and carbanilide alone are formed. W. A. D.

Conversion of Nitrobenzene into *o*-Nitrophenol by means of Caustic Potash. By ALFRED WOHL (*Ber.*, 1899, 32, 3486—3488).—When nitrobenzene is mixed with five times its weight of dry, finely-powdered potassium hydroxide, and the mixture heated in a closed vessel, in small quantities at a time, for 2 hours at 60 — 70° and then for 1 hour at 95° , 33 per cent. of the nitrobenzene is converted into *o* nitrophenol. If the heating at 95° is omitted, about 55 per cent. of the nitrobenzene is recovered unchanged, but of the rest, 45 per cent. is converted into *o*-nitrophenol. The air is not concerned in the oxidation, for this takes place equally in a current of hydrogen. None of the ordinary products of the reduction of nitrobenzene can be detected in the product of the reaction. C. F. B.

Reactions of Phenyl Chloroacetate. By ALBERT MOREL (*Bull. Soc. Chim.*, 1899, [iii], 21, 958—964).—Phenyl chloroacetate, obtained by heating together molecular proportions of phenol and chloroacetyl chloride, crystallises in colourless needles melting at 44 — 45° and is somewhat unstable, exposure to moist air slowly converting it into phenol and chloroacetic acid. It does not react with phenol at 250° , and is the only product of the action of chloroacetyl chloride on phenol, even at 200° ; but when heated with ethyl alcohol or sodium ethoxide, the theoretical amount of ethyl chloroacetate is formed, with liberation of phenol. The replacement of the phenoxy-group in phenyl chloroacetate is therefore effected much more readily than is

the case with phenyl chlorocarbonate (Abstr., 1899, i, 875), whilst the chlorine atom, on the other hand, possesses great stability. The action of ammonia on phenyl chloroacetate in ethereal solution results in the formation of chloroacetamide and ammonium phenoxide. The production of phenyl aminoacetate by heating phenyl chloroacetate with alcoholic ammonia at 140° , as described by Prévost (*J. pr. Chem.*, 1871, [ii], 4, 379), could not be confirmed, and the formation of such a compound seems impossible in view of the reactions described above. N. L.

Reactions of Phenyl Chloroacetate and Phenyl Glycollate. By ALBERT MOREL (*Bull. Soc. Chim.*, 1899, [iii], 21, 964—969. Compare preceding abstract).—When heated with aniline (2 mols.) at 80° , phenyl chloroacetate is converted into *phenyl anilinoacetate*, $\text{NHPh}\cdot\text{CH}_2\cdot\text{CO}_2\text{Ph}$, which crystallises in small, colourless scales melting at $82\text{--}83^{\circ}$, and is soluble in alcohol, ether, chloroform, benzene, or strong acids; boiling with alcohol converts it into ethyl anilinoacetate, with liberation of phenol. If, however, phenyl chloroacetate is boiled with aniline, anilinoacetoanilide is formed. Phenyl chloroacetate reacts with phenylhydrazine at 50° to form *phenyl phenylhydrazinoacetate*, $\text{N}_2\text{H}_2\text{Ph}\cdot\text{CH}_2\cdot\text{CO}_2\text{Ph}$, which crystallises in small, colourless scales melting at $93\text{--}94^{\circ}$. Pyridine slowly enters into combination with phenyl chloroacetate and yields a yellowish-white, unstable compound, $\text{CH}_2\text{Cl}\cdot\text{CO}_2\text{Ph}\cdot\text{C}_5\text{NH}_5$, which is readily decomposed by water. Sodium phenoxide is without action on phenyl chloroacetate in the cold, but on heating a good yield of *phenyl phenoxyacetate* is obtained; this crystallises in slender, colourless, monoclinic needles melting at 58° , and is converted by boiling with alcohol into the corresponding ethyl ester, with liberation of phenol. When treated with ammonia in ethereal solution, it yields phenoxyacetamide, whilst boiling with aniline converts it into phenoxyacetanilide. Excess of ammonia or of aniline at 200° has no action on the second phenoxy-group, and in this respect phenyl phenoxyacetate differs greatly from diphenyl carbonate. From these results, it appears that chloroacetyl chloride, phenyl chloroacetate, and phenyl phenoxyacetate, on the one hand, and carbonyl chloride, phenyl chlorocarbonate, and diphenyl carbonate, on the other, belong to two distinct classes, the first being derived from a substance of complex function, whilst the second includes derivatives of a symmetrical compound. N. L.

Action of Chlorodinitrobenzene on Potassium Benzoate and on Acetamide. By OTTO KYM (*Ber.*, 1899, 32, 3539—3540).—Dinitrophenyl benzoate (Abstr., 1899, i, 647) is produced when potassium benzoate is heated with chlorodinitrobenzene at 180° , although no action occurs in a boiling alcoholic solution. Similarly, chlorodinitrobenzene and acetamide do not interact in alcoholic solution, but when heated together at $200\text{--}210^{\circ}$ give dinitroaniline; in presence of sodium acetate, dinitrophenol is produced. T. M. L.

Ethers of Isonitrosoguaiacol in their Relation to the Space Isomerism of Nitrogen. By JOHN L. BRIDGE and W. CONGER MORGAN (*Amer. Chem. J.*, 1899, 22, 484—488).—The authors have

repeated the work of Pfob (Abstr., 1898, i, 71) and of Rupe (*ibid.*, i, 72) in the hope of isolating stereoisomeric forms of the ethers of isonitrosoguaiacol analogous with the stereoisomeric ethers of toluquinone-*m*-oxime (Abstr., 1899, i, 130, and this vol., i, 103); such space-isomerides do not, however, appear to exist.

The *benzoyl* derivative, $C_{14}H_{11}O_4N$, of isonitrosoguaiacol crystallises from alcohol in straw-coloured, dendritic crystals, and when heated begins to decompose at 175° , and melts at 185 — 188° ; the *dibromide*, $C_{14}H_{11}O_4NBr_2$, is a yellowish-white substance which melts and decomposes at 153 — 154° , and cannot be purified by crystallisation owing to decomposition occurring.

Bromoisonitrosoguaiacol, $C_{14}H_{10}O_4NBr$, prepared by boiling the dibromide with alcohol, crystallises from the latter in well-defined prisms and melts and decomposes at 178° . W. A. D.

Relation between the Structure of Metaphenol [*m*-Hydroxybenzyl] Haloids and their Behaviour towards Alkalis. By KARL AUWERS (*Ber.*, 1899, 32, 3583—3587).—The compounds $OH \cdot C_6Br_3H \cdot CH_2X$ ($X = Cl, Br, I$) [$CH_2X : OH : Br_3 = 1 : 3 : 2 : 4 : 6$], $OH \cdot C_6Br_4 \cdot CH_2Br$ [$= 3 : 2 : 4 : 5 : 6 : 1$]; $OH \cdot C_6Br_3(CH_2X) \cdot CH_2 \cdot OR$ ($X = Br, I$; $R = H, Me, Et, Ac$) [$= 4 : 3 : 5 : 6 : 2 : 1$]; $OH \cdot C_6Br_3(CH_2Br)_2$ [$= 5 : 2 : 4 : 6 : 1 : 3$]; $OH \cdot C_6Br_3(CH_2Br) \cdot CH_2 \cdot OMe$ [$= 2 : 3 : 5 : 6 : 4 : 1$]; $OH \cdot C_6Br_2(CH_2 \cdot OR)_2 \cdot CH_2Br$ ($R = H, Me$) [$= 5 : 3 : 6 : 2 : 4 : 1$]; $OH \cdot C_6Br_3(CHBr_2) \cdot CH \cdot Y$ [$Y = O, (OMe)_2, (OEt)_2, (OAc)_2$] [$= 5 : 3 : 4 : 6 : 1 : 2$] all dissolve in cold dilute aqueous sodium hydroxide without appreciably decomposing after 15 minutes; but the compounds $OH \cdot C_6MeBr_2Z \cdot CH_2Br$ ($Z = Br, CH_2 \cdot OMe$) [$= 2 : 1 : 3 : 6 : 5 : 4$]; $OH \cdot C_6MeBr \cdot CH_2Br$ [$= 4 : 1 : 3 : 5 : 6 : 2$]; $OH \cdot C_6Me_2Br \cdot CH_2Br$ [$= 5 : 2 : 4 : 6 : 1$]; $OH \cdot C_6Me_2Br_2 \cdot CH_2X$ ($X = Cl, Br, I$) [$= 5 : 2 : 4 : 3 : 6 : 1$] decompose almost instantaneously under these conditions with loss of the halogen of the CH_2X group. It thus appears that the presence of a methyl group in the nucleus of a *m*-phenol haloid renders the latter very sensitive to the action of alkalis, although if a hydrogen atom of the methyl group is replaced by a negative radicle, such as OH, OMe, OEt, or OAc, this influence is no longer exercised; those *m*-phenol haloids which contain two methyl groups are much more rapidly decomposed than those containing only one. W. A. D.

Degradation of Phenols during Bromination. By KARL AUWERS and O. ANSELMINO (*Ber.*, 1899, 32, 3587—3597).—Although homologues of phenol yield normal substitution derivatives when heated with bromine in sealed tubes, they yield bromo-derivatives of the next lower homologue when treated with bromine in an open vessel, the methyl group in the *p*-position relative to the hydroxyl being replaced by a bromine atom; in no case, however, has the replacement of an ortho- or meta-methyl group been observed. The alkyl ethers and acetyl derivatives of phenols behave towards bromine in like manner. It appears that the elimination of a methyl group under the conditions cited depends on atmospheric moisture, since when this is excluded normal substitution occurs; by adding a small quantity of water or aqueous hydrobromic acid, the displacement of a methyl radicle is greatly accelerated.

When dibromo- ψ -cumenol or dibromo- p -hydroxy- ψ -cumyl bromide is left in contact with an excess of bromine for 4 hours at the ordinary temperature, it is converted into tribromo- p -xylenol [$\text{OH}:\text{Me}_2 = 1:2:5$]. When ψ -cumenol tribromide (m.p. 128°) is treated similarly, it gives rise after $1\frac{1}{2}$ hours to the compound $\text{CH}_2\text{Br}\cdot\text{C}\begin{smallmatrix} \text{C}(\text{CH}_2\text{Br})\cdot\text{CBr} \\ \text{CBr}\text{---}\text{CMe} \end{smallmatrix}\text{C}\cdot\text{OH}$ (this vol., i, 162), but after 5 hours 2:5:6-tribromo-3-hydroxy- p -xylyl bromide alone is obtained; this crystallises from light petroleum in slender, lustrous needles, melts at $118\text{--}119^\circ$, yields tribromo- p -xylenol (m. p. $178\text{--}179^\circ$) on reduction with zinc dust and acetic acid, and is converted by the further action of bromine into an intractable resin.

Pentabromo- ψ -cumenol [$\text{OH}:\text{Br}_2:(\text{CH}_2\text{Br})_3 = 5:3:6:1:2:4$] is stable towards bromine at the ordinary temperature, but at 100° , in presence of a small quantity of aqueous hydrobromic acid, yields tribromo- p -xylylene bromide, $\text{OH}\cdot\text{C}\begin{smallmatrix} \text{CBr}\cdot\text{C}(\text{CH}_2\text{Br}) \\ \text{C}(\text{CH}_2\text{Br})\cdot\text{CBr} \end{smallmatrix}\text{CBr}$, which crystallises from glacial acetic acid in small, white, silky needles ($+ \text{C}_2\text{H}_4\text{O}_2$), which slowly effloresce and then melt at 184° ; it is insoluble in aqueous alkalis, and yields an *acetyl* derivative, $\text{C}_{10}\text{H}_7\text{O}_2\text{Br}_5$, which crystallises from glacial acetic acid in asbestos-like fibres and melts at 162° .

Tribromo- o -xylenol [$\text{Me}_2:\text{OH} = 1:2:4$], when left with bromine at the ordinary temperature, gives rise after 3 hours to tetrabromo- m -cresol; the tetrabromide, $\text{OH}\cdot\text{C}_6\text{Br}_3\text{Me}\cdot\text{CH}_2\text{Br}$ [$\text{Me}:\text{CH}_2\text{Br}:\text{OH} = 1:2:4$], and the pentabromide, $\text{OH}\cdot\text{C}_6\text{Br}_3(\text{CH}_2\text{Br})_2$ [$(\text{CH}_2\text{Br})_2:\text{OH} = 1:2:4$], derived from o -xylenol yield, on being warmed with bromine for an hour, tetrabromo- m -hydroxybenzyl bromide (this vol., i, 162). Tribromo- m -xylenol [$\text{Me}_2:\text{OH} = 1:3:4$] probably gives rise initially to the bromide $\text{OH}\cdot\text{C}_6\text{MeBr}_3\cdot\text{CH}_2\text{Br}$ [$\text{Me}:\text{CH}_2\text{Br}:\text{OH} = 1:2:4$], but subsequently yields tetrabromo- o -cresol (Bodroux, Abstr., 1898, i, 641), which can also be obtained by heating o -cresol with bromine during 4 hours at 100° . Tribromo- p -hydroxy- m -xylylene bromide [$(\text{CH}_2\text{Br})_2:\text{OH} = 1:3:4$] is stable towards bromine at the ordinary temperature, but on digesting for several hours at 100° with an excess of bromine containing aqueous hydrobromic acid, yields tetrabromo- o -hydroxybenzyl bromide, which is also obtained by heating o -cresol with bromine for 8 hours at 100° ; this crystallises from glacial acetic acid or light petroleum in needles and melts at $158\text{--}159^\circ$.

Tetrabromo- p -cresol is readily converted by bromine into pentabromophenol, the acetate of which crystallises from glacial acetic acid in lustrous needles and melts at $196\text{--}197^\circ$; whilst 3:5-dibromo-4-hydroxybenzyl bromide (Auwers and Daecke, this vol., i, 164) yields a mixture of tribromo- and tetrabromo-phenol. W. A. D.

Action of Chloroform and Alkali on 1:3:4-Xylenol. By KARL AUWERS (*Ber.*, 1899, 32, 3598—3599).—Reimer's reaction gives abnormal results with 1:3:4-xylenol as with ψ -cumenol (Abstr., 1885, 380; 1886, 143; 1896, i, 420); in addition to 2-hydroxy-4:5-dimethylbenzaldehyde, which crystallises from dilute alcohol in long needles or thin plates and melts at $40\text{--}42^\circ$, there is formed a considerable quantity of the compound $\text{C}_9\text{H}_{10}\text{OCl}_2$, which crystallises from light petroleum, melts at $102\text{--}103^\circ$, and is derived from the aldehyde by the replace-

ment of an oxygen atom by two atoms of chlorine, although being insoluble in alkalis, its structure is uncertain. W. A. D.

Oxidation Products of Phenols and Bromophenols and the Constitution of the Isomeric Tribromo- ψ -cumenol. By KARL AUWERS (*Ber.*, 1899, 32, 3440—3453).—A theoretical discussion of the compounds described in the following three abstracts.

R. H. P.

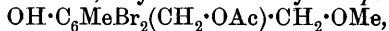
Oxidation Product of Pseudocumenol Tribromide [Tribromo- ψ -cumenol]. By KARL AUWERS and A. EBNER (*Ber.*, 1899, 32, 3454—3465).—On treating tribromo- ψ -cumenol with a mixture of nitric and acetic acids, an oxy-compound, $\text{CO} \begin{smallmatrix} \text{CBr}:\text{CMe} \\ \text{CMe}:\text{CBr} \end{smallmatrix} \text{C}(\text{OH})\cdot\text{CH}_2\text{Br}$, is obtained, which crystallises in compact prisms melting at 158° , on reduction yields dibromo- ψ -cumenol, and by acetic anhydride is converted into the diacetate of dibromo- p -hydroxy- ψ -cumyl alcohol. The corresponding *acetyl* derivative, $\text{OAc}\cdot\text{C}_6\text{Me}_2\text{Br}_2\text{O}\cdot\text{CH}_2\text{Br}$, obtained by treatment with acetyl chloride, forms compact, white crystals melting at 118 — 119° . On treating the oxy-compound dissolved in methyl alcohol with caustic soda and acidifying, an *oxide*, $\text{CO} \begin{smallmatrix} \text{CBr}:\text{CMe} \\ \text{CMe}:\text{CBr} \end{smallmatrix} \text{C} \begin{smallmatrix} \text{O} \\ \diagup \\ \text{CH}_2 \end{smallmatrix}$, is precipitated; it crystallises in long needles melting at 109 — $110\cdot5^\circ$, and with acetyl bromide yields an isomeric *acetyl* derivative, $\text{C}_6\text{Me}_2\text{Br}_3\text{O}\cdot\text{CH}_2\cdot\text{OAc}$, which crystallises in white leaflets melting at 103° . The *diacetate*, $\text{OAc}\cdot\text{C}_6\text{Me}_2\text{Br}_2\cdot\text{CH}_2\cdot\text{OAc}$, obtained by treating the acetyl derivative (m. p. 119°) with zinc dust and acetic acid, or the acetyl derivative (m. p. 103°) with sodium acetate and acetic acid, forms white leaflets melting at 95° . With acetyl chloride, the oxide forms an *additive* compound, $\text{C}_6\text{Me}_2\text{Br}_2\text{ClO}\cdot\text{CH}_2\cdot\text{OAc}$, which crystallises in small needles melting at 96 — 98° .

The *monomethyl ether* of dibromo- p -hydroxy- ψ -cumylene *o*-glycol, $\text{OH}\cdot\text{C} \begin{smallmatrix} | \\ \text{CMe} \end{smallmatrix} \text{—CBr}:\text{C} \begin{smallmatrix} | \\ \text{CMe} \end{smallmatrix} \text{CH}_2\cdot\text{OMe}$, obtained by treating the oxy-compound with methyl alcohol and sodium hydroxide, forms small needles melting at 149° ; the corresponding *monoethyl ether* melts at 113 — 114° . The *diacetate* of the methyl ether is obtained by the action of acetic anhydride, and forms yellowish prisms melting at 107 — 108° .

3:6-Dibromo-5-hydroxy- ψ -cumylene dibromide, $\text{OH}\cdot\text{C}_6\text{MeBr}_2(\text{CH}_2\text{Br})_2$, prepared by the action of hydrogen bromide on the methyl ether just described, forms compact, short needles melting at 151 — 152° , and is insoluble in alkalis. The *acetyl* derivative forms lustrous needles melting at 132 — 133° . If a concentrated solution of the dibromide in methyl alcohol is left for some time, the portion which can be precipitated by water is soluble in alkalis, and is the *methyl ether* of 3:6-dibromo-5-hydroxy- ψ -cumylene bromohydrin, $\text{OH}\cdot\text{C}_6\text{MeBr}_2(\text{CH}_2\text{Br})\cdot\text{CH}_2\cdot\text{OMe}$, which forms short needles melting at 107 — 108° ; on reduction, it yields the *methyl ether*, $\text{OH}\cdot\text{C}_6\text{Me}_2\text{Br}_2\cdot\text{CH}_2\cdot\text{OMe}$, melting at 92° .

By the continued action of methyl alcohol on the dibromide, 3:6-dibromo-5-hydroxy- ψ -cumylene *dimethyl ether* is obtained, crystallising in compact prisms melting at 79 — 80° ; it is converted by the action

of hydric hydrogen chloride into the *methyl* ether of the chlorohydrin, $\text{OH} \cdot \text{C}_6\text{MeBr}_2(\text{CH}_2\text{Cl}) \cdot \text{CH}_2 \cdot \text{OMe}$, which melts at $93-95.5^\circ$; on treatment with sodium acetate, it yields the *acetyl compound*,



which forms white leaflets melting at $110-111^\circ$.

R. H. P.

Dibromo-*m*-hydroxy- ψ -cumyl Bromide. By KARL AUWERS and TH. MAAS (*Ber.*, 1899, 32, 3466—3475. Compare *Abstr.*, 1898, i, 343).—

3 : 6-Dibromo-5-hydroxy- ψ -cumyl bromide, $\text{CMe} \begin{smallmatrix} \text{C}(\text{OH}) \cdot \text{CBr} \\ \text{CBr} = \text{CMe} \end{smallmatrix} \text{C} \cdot \text{CH}_2\text{Br}$,

prepared by treating the diacetate of 3 : 6-dibromo-5-hydroxy- ψ -cumyl alcohol with hydrogen bromide, crystallises in long, silky needles melting at 128° , and forms an *acetyl* derivative melting at $105-106^\circ$. On boiling with alcohol, it yields the *ethyl* ether of 3 : 6-dibromo-5-hydroxy- ψ -cumyl alcohol melting at $63-64^\circ$. The *acetyl* derivative of the corresponding methyl derivative melts at $80-81^\circ$. The diacetate first mentioned, on reduction with sodium amalgam, yields the *diacetate* of 3-bromo-5-hydroxy- ψ -cumyl alcohol, which forms colourless prisms melting at 65° . The *monoacetate*, obtained when the reduction is effected with zinc dust and acetic acid, crystallises in small needles melting at 104° . Both acetates, on hydrolysis, yield the 3-bromo-5-hydroxy- ψ -cumyl alcohol, which forms lustrous, white leaflets melting at 164° . 5-Hydroxy- ψ -cumyl alcohol, prepared by the reduction of 3 : 6-dibromo-5-hydroxy- ψ -cumyl alcohol with sodium amalgam, crystallises in lustrous leaflets melting at 153° , and with bromine yields 6-bromo-5-hydroxy- ψ -cumyl bromide, which forms long needles melting at 116° , and with sodium acetate yields the *acetyl* derivative of the corresponding alcohol melting at 103° . R. H. P.

Oxidation Products of Phenols and Bromophenols. By KARL AUWERS and J. BROICHER [and in part W. WOLFF] (*Ber.*, 1899, 32, 3475—3486. Compare preceding abstracts and *Abstr.*, 1898, i, 30).—

The *acetyl* derivative, $\text{CO} \begin{smallmatrix} \text{CMe} \cdot \text{CBr} \\ \text{CMe} \cdot \text{CBr} \end{smallmatrix} \text{CMe} \cdot \text{OAc}$, obtained by treating the oxy-compound of dibromomesitol with acetic anhydride, forms rhombohedra melting at $94-95^\circ$. The oxy-compound of 3 : 5 : 6-tribromo-1 : 2 : 4-xylenol forms a *monoacetate* melting at $116-117^\circ$, and a *diacetate* melting at $101-102^\circ$, which, on treatment with hydrogen bromide, yields ω : 2 : 5 : 6-tetrabromo-1 : 3 : 4-xylenol, melting at $138-139^\circ$ and forming an *acetyl* derivative which melts at $110-111^\circ$. The constitution of the tetrabromo-compound is proved by its preparation in several stages from ω : 3 : 5 : 6-pentabromo-1 : 2 : 4-xylenol.

the *methyl* ether, $\text{OH} \cdot \text{C} \begin{smallmatrix} \text{CMe} \cdot \text{CBr} \\ \text{CBr} \cdot \text{CBr} \end{smallmatrix} \text{C} \cdot \text{CH}_2 \cdot \text{OMe}$
 $\text{CBr} \cdot \text{CBr} \cdot \text{C} \cdot \text{CH}_2 \cdot \text{OH}$, melting at $176-178^\circ$
 being obtained as an intermediate product.

ω : 2 : 4 : 5 : 6-Pentabromocresol, obtained by the action of bromine on the tetrabromo-compound, forms silky needles melting at $136-137^\circ$.

The following derivatives of tribromomesitol were prepared in a similar manner to those of tribromo- ψ -cumenol (see preceding abstracts).

An oxy-compound, $\text{CO} \begin{smallmatrix} \text{CMe} \cdot \text{CBr} \\ \text{CMe} \cdot \text{CBr} \end{smallmatrix} \text{C}(\text{OH}) \cdot \text{CH}_2\text{Br}$, which crystallises

in prisms melting at 145—146° and forms an *acetyl* derivative melting at 126—127°, and the corresponding *oxide*, which forms compact needles, melting at 118—119°.

ω : 3 : 5 : 6-Pentabromo-1 : 2 : 4-xylenol yields an *oxy*-compound which crystallises in lustrous, monoclinic prisms melting at 188—190° and forms an *acetyl* derivative melting at 145—146°. R. H. P.

Preparation of Aromatic Thiols. By EDOUARD BOURGEOIS (*Rec. Trav. Chim.*, 1899, 18, 426—450).—The author describes improvements in the working of the two methods used for the preparation of aromatic thiols: the reduction of aromatic sulphochlorides, and the hydrolysis of aromatic derivatives of xanthogenic acid.

Phenyl mercaptan, prepared by the first method, has no alliaceous odour and boils at 169·5° under 760 mm. pressure.

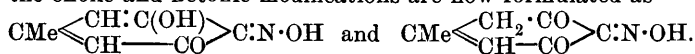
p-Tolyl mercaptan boils at 195° under 760 mm. pressure (Vallin gave 194°).

β -Naphthyl mercaptan boils under the ordinary pressure at 288° with partial decomposition into di- β -naphthyl sulphide and hydrogen sulphide; it is slightly volatile in steam, not non-volatile as stated in Beilstein.

m-Tolyl mercaptan boils at 195·4° under 760 mm. pressure and has a specific gravity 1·06251 at 0°/4°. T. H. P.

Constitution of Mononitrosoorcinol. By FERDINAND HENRICH (*Ber.*, 1899, 32, 3419—3424. Compare *Abstr.*, 1897, i, 446).—Nitrosoorcinol is the oxime of an orthoquinone, and not of a paraquinone as has been previously assumed; the aminophenol formed on reducing the monomethyl ether of nitrosoorcinol readily gives an *acetyl* derivative, $\text{NHAc} \cdot \text{C}_6\text{H}_2\text{Me}(\text{OMe}) \cdot \text{OH}$, which crystallises from dilute alcohol in needles and melts at 156—157°; when this is heated, it undergoes ortho-condensation and gives *methoxy- μ -methyltoluoxazole*, $\text{OMe} \cdot \text{C}_6\text{H}_2\text{Me} \langle \text{N} \rangle \text{CMe}$, which crystallises from alcohol, melts at 71·5—72°, and when heated under pressure with concentrated hydrochloric acid gives aminoorcinol hydrochloride, methyl chloride, and acetic acid. This view is confirmed by a comparison of the monomethyl ether of nitrosoorcinol with Kietaihl's two nitroso-derivatives from resorcinol monomethyl ether (*Abstr.*, 1899, i, 343), since it closely resembles the ortho-derivative in physical and chemical properties; a green *labile modification* of the latter has been obtained which passes sharply into the stable yellow modification when heated to 120°.

Of the two possible formulæ for nitrosoorcinol, the diortho-formula is preferred, since substitution takes place most readily in this position, and the enolic and ketonic modifications are now formulated as



T. M. L.

Action of Methylene Sulphate on Benzyl Alcohol. By MARCEL DELÉPINE (*Bull. Soc. Chim.*, 1899, [iii], 21, 1059—1061).—The action of methylene sulphate on benzyl alcohol at 60—65° results

in the formation of dibenzylformal and benzyl hydrogen sulphate. *Dibenzylformal*, $\text{CH}_2(\cdot\text{O}\cdot\text{CH}_2\text{Ph})_2$, is a colourless liquid of faint benzylic odour, boils at about 330° and does not solidify at -23° ; it is resinified by concentrated sulphuric acid, and is converted into benzyl iodide by the action of fuming hydriodic acid. *Benzyl hydrogen sulphate* itself could not be prepared in the pure state, since its aqueous solution becomes resinified on evaporation. The *barium* salt, $\text{Ba}(\text{SO}_4\cdot\text{CH}_2\text{Ph})_2 + 2\text{H}_2\text{O}$, crystallises from water in long, colourless needles; the anhydrous salt, obtained by cooling a solution in 80 per cent. alcohol, slowly resinifies on keeping and decomposes when heated even below 80° ; its aqueous solution deposits barium sulphate when concentrated by heat. The *potassium* salt crystallises from alcohol in anhydrous, slender needles which are stable below 100° . The *silver* and *lead* salts undergo decomposition when their aqueous solutions are concentrated, but the greenish *copper* salt, which crystallises with $4\text{H}_2\text{O}$, is more stable.

N. L.

Action of Bromine on *p*-Hydroxybenzyl Alcohol. By KARL AUWERS and S. DAECHE (*Ber.*, 1899, 32, 3373—3381. Compare following abstract).—*p*-Hydroxybenzyl alcohol is best prepared by Hutchinson's method (*Abstr.*, 1891, 561) and crystallises from water in large, colourless prisms or compact needles melting at $124.5\text{--}125.5^\circ$ and not at 110° as stated by Biedermann (*Abstr.*, 1887, 38) and Hutchinson.

3 : 5-Dibromo-4-hydroxybenzyl bromide, $\text{OH}\cdot\text{C}_6\text{H}_2\text{Br}_2\cdot\text{CH}_2\text{Br}$, obtained by the action of an acetic acid solution of bromine on a solution of the hydroxy-alcohol in the same solvent, crystallises from light petroleum in small, colourless needles melting at $149\text{--}150^\circ$; it dissolves readily in cold ether, also in warm benzene or acetic acid, but is insoluble in alkalis. Its constitution follows from the fact that when reduced it yields Werner's dibromo-*p*-cresol (*Bull. Soc. Chim.*, 1886, [ii], 46, 278). The *acetyl* derivative, $\text{OAc}\cdot\text{C}_6\text{H}_2\text{Br}_2\cdot\text{CH}_2\text{Br}$, crystallises from light petroleum in large crystals melting at $76.5\text{--}77.5^\circ$ and is only sparingly soluble in cold methyl or ethyl alcohol. When the tribromide is shaken with acetone and water, it is converted into 3 : 5-dibromo-4-hydroxybenzyl alcohol, $\text{OH}\cdot\text{C}_6\text{H}_2\text{Br}_2\cdot\text{CH}_2\cdot\text{OH}$, which crystallises from benzene in compact, colourless plates melting at $116\text{--}117^\circ$, and is readily soluble in ether or alcohol. The corresponding ethers, $\text{OH}\cdot\text{C}_6\text{H}_2\text{Br}_2\cdot\text{CH}_2\cdot\text{OR}$, are obtained when the tribromide is heated with the requisite alcohol. The *methyl* ether crystallises in glistening needles melting at $71\text{--}72^\circ$, and the *ethyl* ether in small prisms melting at $93.5\text{--}94.5^\circ$. The *acetate*, $\text{OH}\cdot\text{C}_6\text{H}_2\text{Br}_2\cdot\text{CH}_2\cdot\text{OAc}$, obtained by the action of an acetic acid solution of anhydrous sodium acetate on the tribromide, crystallises from light petroleum in compact prisms melting at $114.5\text{--}115.5^\circ$; it dissolves in alkalis, but rapidly undergoes decomposition when the alkali is too strong; it is also decomposed when boiled with different alcohols, yielding the corresponding ethers. The isomeric *acetate*, $\text{OAc}\cdot\text{C}_6\text{H}_2\text{Br}_2\cdot\text{CH}_2\cdot\text{OH}$, is obtained when a solution of the acetyl derivative of 3 : 5-dibromo-4-hydroxybenzyl iodide in acetone is treated with moist silver oxide for several days at the ordinary temperature, and forms a yellowish oil. The *diacetate*,

$\text{OAc} \cdot \text{C}_6\text{H}_2\text{Br}_2 \cdot \text{CH}_2 \cdot \text{OAc}$, crystallises in prisms melting at $68-70^\circ$; it may be obtained by the action of acetic anhydride on the hydroxybenzyl alcohol or on either of the monoacetyl derivatives, and when its acetic acid solution is treated with hydrogen iodide at 80° it yields 3:5-dibromo-4-hydroxybenzyl iodide, which crystallises from benzene in yellow needles melting at $148-149^\circ$; when hydrogen iodide is employed at the ordinary temperature, the product is the *acetyl* derivative, $\text{OAc} \cdot \text{C}_6\text{H}_2\text{Br}_2 \cdot \text{CH}_2\text{I}$, which crystallises in colourless needles melting at $94-95^\circ$. J. J. S.

Action of Bromine on *m*-Hydroxybenzyl Alcohol. By KARL AUWERS AND W. RICHTER (*Ber.*, 1899, 32, 3381—3384. Compare Abstr., 1897, i, 335, 336, and preceding abstract).—When a warm acetic acid solution of *m*-hydroxybenzyl alcohol, which is best obtained by von den Velden's method (*Journ.*, 1877, ii, 338), is treated with bromine also dissolved in acetic acid, 2:4:6-tribromo-3-hydroxybenzyl bromide, $\text{OH} \cdot \text{C}_6\text{HBr}_3 \cdot \text{CH}_2\text{Br}$, is formed; it crystallises in small needles melting at 149° , and dissolves readily in alkalis, and in most organic solvents except light petroleum. On reduction with zinc dust and acetic acid, it yields Claus and Hirsch's tribromo-*m*-cresol melting at 84° (Abstr., 1889, 389). Its *acetyl* derivative crystallises in glistening needles and melts at 104° .

Tribromohydroxybenzyl acetate, $\text{OH} \cdot \text{C}_6\text{HBr}_3 \cdot \text{CH}_2 \cdot \text{OAc}$, forms small needles melting at 133° ; when hydrolysed with alcoholic sodium hydroxide, it yields 2:4:6-tribromo-3-hydroxybenzyl alcohol, melting at 130° ; this is not readily converted into its ethers by the action of different alcohols.

The diacetate, $\text{OAc} \cdot \text{C}_6\text{HBr}_3 \cdot \text{CH}_2 \cdot \text{OAc}$, crystallises from a mixture of ether and light petroleum in small prisms melting at $83-84^\circ$.

2:4:6-Tribromo-3-hydroxybenzyl chloride, obtained by the action of dry hydrogen chloride on a hot acetic acid solution of the alcohol, crystallises in needles melting at 133° , and the iodide, obtained by shaking an alcoholic solution of the bromide with a concentrated aqueous solution of potassium iodide, crystallises in glistening, feathery needles melting at 146° . J. J. S.

Tribromo-derivatives of ψ -Cumenol and Mesityl. By KARL AUWERS, F. A. TRAUN, and R. WELDE (*Ber.*, 1899, 32, 3297—3309. Compare this vol., i, 96; and Abstr., 1897, i, 34 and 335; 1898, i, 646; 1899, i, 343).—The *acetyl* derivative, $\text{OAc} \cdot \text{C}_6\text{Me}_2\text{Br}_2 \cdot \text{CH}_2 \cdot \text{OMe}$, prepared from 3:6-dibromo-4-hydroxy- ψ -cumyl methyl ether, crystallises from light petroleum or glacial acetic acid in white needles, melts at $114-114.5^\circ$, and is not acted on by gaseous hydrogen chloride in boiling acetic acid solution; at 150° , or in presence of zinc chloride at 100° , hydrogen chloride converts the acetate into the chloride, $\text{OH} \cdot \text{C}_6\text{Me}_2\text{Br}_2 \cdot \text{CH}_2\text{Cl}$, which melts at 110° , and yields an *acetyl* derivative crystallising in white needles and melting at $150-150.5^\circ$. Hydrogen bromide converts the *acetyl* derivative melting at $114-114.5^\circ$ into dibromo-*p*-acetoxy- ψ -cumyl bromide, $\text{OAc} \cdot \text{C}_6\text{Me}_2\text{Br}_2 \cdot \text{CH}_2\text{Br}$, which melts at 161° , and on reduction with zinc dust and acetic acid yields the *acetyl* derivative, $\text{OAc} \cdot \text{C}_6\text{Me}_3\text{Br}_2$, melting at $80.5-81^\circ$, derived from

dibromo-*p-ψ*-cumenol; hydrogen iodide behaves similarly, giving rise to dibromo-*p*-acetoxy-*ψ*-cumyl iodide, $\text{OAc} \cdot \text{C}_6\text{Me}_2\text{Br}_2 \cdot \text{CH}_2\text{I}$, which crystallises from glacial acetic acid in felted needles, melts at $174-175^\circ$, and can also be obtained by the action of hydrogen iodide on the diacetate melting at $105-106^\circ$, derived from dibromo-*p*-hydroxy-*ψ*-cumyl alcohol. The iodide is converted by moist silver oxide into the corresponding alcohol, $\text{OAc} \cdot \text{C}_6\text{Me}_2\text{Br}_2 \cdot \text{CH}_2 \cdot \text{OH}$, which melts at $122-122.5^\circ$ (Auwers and Sheldon, Abstr., 1898, i, 647); this is not acted on by boiling alcohol or aqueous acetone, but is hydrolysed by alcoholic potash to dibromo-*p*-hydroxy-*ψ*-cumyl alcohol (m. p. 166°).

The isomeric acetate, $\text{OH} \cdot \text{C} \begin{smallmatrix} \text{CBr} \cdot \text{CMe} \\ \text{CMe} \cdot \text{CBr} \end{smallmatrix} \text{C} \cdot \text{CH}_2 \cdot \text{OAc}$ (m. p. 114°),

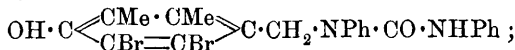
which is prepared by the action of sodium acetate on *ψ*-cumenol bromide and is insoluble in alkalis, is, on the other hand, hydrolysed instantaneously by alcohol or aqueous acetone. When dibromo-*p*-acetoxy-*ψ*-cumyl iodide is heated with silver oxide in benzene solution, it is converted into the ether, $(\text{OAc} \cdot \text{C}_6\text{Me}_2\text{Br}_2 \cdot \text{CH}_2)_2\text{O}$ (Auwers and Avery, Abstr., 1896, i, 150). 2:6-Dibromo-4-hydroxymesityl methyl ether, $\text{OH} \cdot \text{C}_6\text{Me}_2\text{Br}_2 \cdot \text{CH}_2 \cdot \text{OMe}$, prepared by heating mesitol tribromide with methyl alcohol, crystallises in thick, monoclinic plates, and melts at 142° ; the acetyl derivative crystallises from dilute acetic acid in small plates, melts at $109-110^\circ$, and is converted by hydrogen iodide into 2:6-dibromo-4-acetoxymesityl iodide, $\text{OAc} \cdot \text{C}_6\text{Br}_2\text{Me}_2 \cdot \text{CH}_2\text{I}$, which separates from glacial acetic acid or acetone in slender, silky needles, and melts at $176-177^\circ$. 2:6-Dibromo-4-acetoxymesityl alcohol, $\text{OAc} \cdot \text{C}_6\text{Br}_2\text{Me}_2 \cdot \text{CH}_2 \cdot \text{OH}$, prepared by decomposing the iodide with aqueous acetone, crystallises from light petroleum in felted needles, melts at 128° , and is converted by alcoholic potash into 2:6-dibromo-4-hydroxymesityl alcohol (m. p. 186°); with acetic anhydride, it yields the diacetate (m. p. $159-160^\circ$), whilst hydrogen bromide converts it into 2:6-dibromo-4-acetoxymesityl bromide, $\text{OAc} \cdot \text{C}_6\text{Me}_2\text{Br}_2 \cdot \text{CH}_2\text{Br}$ (m. p. $150-151^\circ$).

In the light of these results, the structure of the acetyl derivatives obtained by the action of sodium acetate on phenol bromides which are insoluble in aqueous alkali is discussed; these must be regarded as similar in structure to the corresponding phenol bromides, and therefore, like the latter, can be represented by three formulæ (compare this vol., i, 96) which cannot as yet be differentiated.

The phenylurethane, $\text{CH}_2\text{Br} \cdot \text{C}_6\text{Me}_2\text{Br}_2 \cdot \text{O} \cdot \text{CO} \cdot \text{NHPh}$, formed by the action of phenylcarbimide on mesitol tribromide (compare Auwers and Allendorff, Abstr., 1899, i, 32), melts and decomposes at 257° ,* and on reduction with zinc dust and acetic acid is converted into the phenylurethane, $\text{C}_6\text{Me}_3\text{Br}_2 \cdot \text{O} \cdot \text{CO} \cdot \text{NHPh}$, of dibromomesitol, which can also be prepared from the latter by the action of phenylcarbimide; this cannot be obtained in well-defined crystals, and melts somewhat indefinitely between 213° and 216° . When the phenylurethane of mesitol tribromide, dissolved in xylene, is heated with aniline (2 mols.), it yields the phenylurethane, $\text{NHPh} \cdot \text{CH}_2 \cdot \text{C}_6\text{Me}_3\text{Br}_2 \cdot \text{O} \cdot \text{CO} \cdot \text{NHPh}$, of 2:6-dibromo-4-hydroxymesitylaniline, which forms short, slender

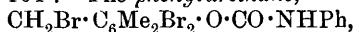
* ? 227° , compare Auwers and Allendorff, *loc. cit.*, who give 226° , and p. 3300 of original.—W. A. D.

needles, melts at 190—194°, and is easily hydrolysed by alcoholic potassium hydroxide to dibromo-*p*-hydroxymesitylaniline (m. p. 136°). The latter substance, when treated with phenylcarbimide, gives rise to a *phenylurethane* which readily dissolves in aqueous alkalis, is isomeric, not identical, with the phenylurethane melting at 190—194°, and hence appears to have the constitution



the phenylcarbimide, in fact, has attacked the anilino- in preference to the hydroxyl group, and with *p*-aminophenol a similar behaviour is observed, *p*-hydroxydiphenylcarbamide, $\text{OH} \cdot \text{C}_6\text{H}_4 \cdot \text{NH} \cdot \text{CO} \cdot \text{NHPh}$, being formed; this crystallises from dilute alcohol in lustrous, pearl-grey needles, melts at 216—217°, and is easily soluble in aqueous alkalis. The use of phenylcarbimide as a means of recognising the presence of a hydroxyl group in organic compounds must therefore be limited to compounds which do not contain an amino-radicle.

The *phenylurethane*, $\text{OAc} \cdot \text{CH}_2 \cdot \text{C}_6\text{Me}_2\text{Br}_2 \cdot \text{O} \cdot \text{CO} \cdot \text{NHPh}$, obtained by the action of phenylcarbimide on dibromo-*p*-hydroxymesityl acetate (m. p. 165—166°), prepared from mesitol tribromide and sodium acetate, crystallises from glacial acetic acid in short, slender needles and melts at 163—164°. The *phenylurethane*,

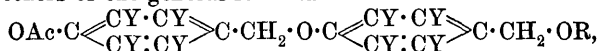


can be obtained only with difficulty from dibromo-*p*-hydroxy- ψ -cumyl bromide, and separates from hot glacial acetic acid as a white powder melting at 225—230°. W. A. D.

Dibromo-*p*-hydroxymesityl Alcohol. By KARL AUWERS and F. A. TRAUN (*Ber.*, 1899, 32, 3309—3317).—4 : 6-Dibromo-2-amino-*m*-xylene, prepared by reducing the corresponding nitro-compound, crystallises from 75 per cent. alcohol in slender, felted needles, melts at 99—100°, and is converted by the diazo-reaction into 4 : 6-dibromo-2-hydroxy-*m*-xylene, which crystallises from light petroleum in slender needles and melts at 132—133°; the *acetate* of the latter separates from alcohol or glacial acetic acid in white leaflets and melts at 79—80°. 2 : 6-Dibromo-4-hydroxymesityl alcohol, $\text{OH} \cdot \text{C}_6\text{Me}_2\text{Br}_2 \cdot \text{CH}_2 \cdot \text{OH}$, prepared from the foregoing hydroxy-compound by the Lederer-Manasse reaction, using formaldehyde and dilute aqueous sodium hydroxide, crystallises from xylene, melts at 186°, and is identical with the compound melting at 191—192° formed by acting with aqueous acetone on mesitol tribromide (the bromide of dibromoanhydro-*p*-hydroxymesityl alcohol, Auwers and Allendorff, *Abstr.*, 1899, i, 32). When the hydroxy-alcohol is heated for several hours at 160—170°, it is converted into *tetrabromo-p-dihydroxydimesityl ether*, $(\text{OH} \cdot \text{C}_6\text{Br}_2\text{Me}_2 \cdot \text{CH}_2)_2\text{O}$, which is nearly insoluble in all the ordinary solvents, melts at 256°, and is identical with the compound formerly stated (Auwers and Allendorff, *loc. cit.*) to be isomeric with the hydroxy-alcohol; the latter conclusion was arrived at because preparations melting at 252°, on being heated with benzene or xylene, appeared to be converted into the hydroxy-alcohol melting at 192°. It is now shown, however, that the impure hydroxy-alcohol, containing small quantities of the ether, when heated, undergoes conversion into the

latter, and melts at 252° , although the pure hydroxy-alcohol, when similarly treated, remains unchanged and melts at 192° . The samples formerly heated with benzene or xylene and supposed to consist of the compound melting at 252° , in reality consisted mostly of the hydroxy-alcohol, and the apparent regeneration of the latter is thus explained. The diacetate of the ether melts at 229° and is identical with the compound prepared by the action of silver oxide on the acetyl derivative of dibromo-*p*-hydroxymesityl bromide (*loc. cit.*); by digestion with methyl iodide and sodium methoxide, the ether yields the *dimethyl* derivative, $\text{O}(\text{C}_6\text{Me}_2\text{Br}_2\cdot\text{OMe})_2$, which crystallises from a mixture of absolute alcohol and benzene in slender, white needles and melts at $205\text{--}206^{\circ}$. W. A. D.

Substituted Phenyl Benzyl Ethers. By KARL AUWERS, F. A. TRAUN, and R. WELDE (*Ber.*, 1899, **32**, 3317—3331).—By the action of sodium alkyl oxides on acetylated hydroxybenzyl haloids of the type $\text{OAc}\cdot\text{C}\begin{smallmatrix} \text{CY}\cdot\text{CY} \\ \text{CY}:\text{CY} \end{smallmatrix}\text{C}\cdot\text{CH}_2\text{X}$, where X represents a halogen and Y any substituent, crystalline compounds are obtained, which the author formerly regarded as stilbene derivatives of the type $\text{OAc}\cdot\text{C}\begin{smallmatrix} \text{CY}\cdot\text{CY} \\ \text{CY}:\text{CY} \end{smallmatrix}\text{C}\cdot\text{CH}:\text{CH}\cdot\text{C}\begin{smallmatrix} \text{CY}\cdot\text{CY} \\ \text{CY}:\text{CY} \end{smallmatrix}\text{C}\cdot\text{OAc}$ (*Annalen*, 1898, **301**, 260), but are shown in the present paper to be substituted phenylbenzyl ethers of the general formula



R denoting the alkyl radicle.

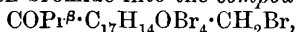
The *ether*, $\text{OAc}\cdot\text{C}_6\text{Me}_2\text{Br}_2\cdot\text{CH}_2\cdot\text{O}\cdot\text{C}_6\text{Me}_2\text{Br}_2\cdot\text{CH}_2\cdot\text{OEt}$, prepared by the action of alcoholic sodium ethoxide on dibromo-*p*-acetoxy- ψ -cumyl bromide, melts at $175\text{--}176^{\circ}$, and has been already described as tetrabromodiacetoxytetramethylstilbene (Auwers and Sheldon, *Annalen*, 1898, **301**, 272); the corresponding *ether*, $\text{C}_{22}\text{H}_{24}\text{O}_4\text{Br}_4$, prepared from dibromo-*p*-acetoxyimesityl bromide (Auwers and Allendorff, *Abstr.*, 1899, i, 32) melts at $217\text{--}218^{\circ}$. The former of these is converted by gaseous hydrogen bromide in glacial acetic acid solution at 80° into the *ether*, $\text{OAc}\cdot\text{C}_{17}\text{H}_{14}\text{OBr}_4\cdot\text{CH}_2\text{Br}$, which crystallises from glacial acetic acid or xylene in needles and melts at $219\text{--}221^{\circ}$; at 100° , or more rapidly at the boiling point of acetic acid, ψ -cumenol tribromide (m. p. 126°) is formed. The isomeric mesitol derivative, melting at $217\text{--}218^{\circ}$, gives rise under similar conditions to the *ether* $\text{C}_{20}\text{H}_{19}\text{O}_3\text{Br}_5$, which crystallises from xylene in needles and melts at $254\text{--}255^{\circ}$. The *ether*, $\text{OAc}\cdot\text{C}_{17}\text{H}_{14}\text{OBr}_4\cdot\text{CH}_2\text{I}$, prepared by the action of hydrogen iodide on the ψ -cumyl derivative melting at $175\text{--}176^{\circ}$ melts and decomposes at $219\text{--}221^{\circ}$, and cannot be crystallised from xylene or benzene without decomposition occurring; at 100° , hydrogen iodide gives rise to dibromo-*p*-hydroxy- ψ -cumyl iodide, although hydrogen chloride, under similar conditions, is without action, and only begins to act at 150° , when dibromo-*p*-hydroxy- ψ -cumyl chloride is formed.

The *methyl ether*, $\text{OAc}\cdot\text{C}_{17}\text{H}_{14}\text{OBr}_4\cdot\text{CH}_2\cdot\text{OMe}$, prepared by the action of sodium methoxide on dibromo-*p*-acetoxy- ψ -cumyl bromide, crystallises from glacial acetic acid in slender needles and melts at $202\text{--}204^{\circ}$.

whilst the isomeric *mesityl* derivative crystallises similarly, melts at 220—221°, and can also be obtained by the interaction of dibromo-*p*-hydroxymesityl methyl ether with sodium methoxide and dibromo-*p*-acetoxyesitylbromide. The latter fact shows that the action of sodium alkyl oxides on acetylated hydroxybenzyl haloids takes place in two stages. Hydrogen bromide converts the mesityl derivative, melting at 220—221°, into the bromide, $\text{OAc}\cdot\text{C}_{17}\text{H}_{14}\text{OBr}_4\cdot\text{CH}_2\text{Br}$, already described.

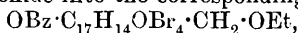
The *amyl ether*, $\text{OAc}\cdot\text{C}_{17}\text{H}_{14}\text{OBr}_4\cdot\text{CH}_2\cdot\text{OC}_5\text{H}_{11}$, crystallises from glacial acetic acid in slender needles and melts at 146—147°; the isomeric *mesityl* compound has similar properties, and melts at 163—164°. Hydrogen bromide interacts with these substances in the same manner as with the analogous ethyl and methyl ethers.

By the action of sodium ethoxide on dibromo-*p*-isobutyroxy- ψ -cumyl bromide (*Annalen*, 1898, 301, 280), small quantities of *dibromo-p-isobutyroxy- ψ -cumyl ethyl ether*, $\text{COPr}^s\cdot\text{O}\cdot\text{C}_6\text{Me}_2\text{Br}_2\cdot\text{CH}_2\cdot\text{OEt}$, melting at 74—75°, are formed, together with a larger proportion of the *ether*, $\text{COPr}^s\cdot\text{C}_{17}\text{H}_{14}\text{OBr}_4\cdot\text{CH}_2\cdot\text{OEt}$, which crystallises from alcohol in white needles and melts at 147—148°; the *mesityl* derivative isomeric with the latter crystallises from glacial acetic acid in silky needles and melts at 182—183°. The ψ -cumyl ether (m. p. 147—148°) is converted by hydrogen bromide into the *compound*



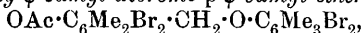
which forms slender needles and melts at 192—193°; the isomeric *mesityl* derivative melts at 221—223°, but was not obtained pure.

The *benzoyl* derivative, $\text{OBz}\cdot\text{C}_6\text{Me}_2\text{Br}_2\cdot\text{CH}_2\text{Br}$, of dibromo-*p*-hydroxymesityl bromide crystallises from glacial acetic acid or petroleum in long, lustrous needles, melts at 160—161°, and is converted by sodium ethoxide into the corresponding *ether*,



which crystallises from benzene or glacial acetic acid in white, felted needles, melts at 222—223°, and when treated with hydrogen bromide gives rise to the corresponding *bromide*, $\text{C}_{25}\text{H}_{21}\text{O}_3\text{Br}_5$, which crystallises from xylene in white needles and melts at 234—235°.

Dibromo-p-acetoxy- ψ -cumyl dibromo-p- ψ -cumyl ether,



prepared by reducing the corresponding bromide (m. p. 219—221°) with zinc dust and acetic acid, crystallises from glacial acetic acid in white, felted needles, melts at 204—205°, and on digestion with sodium methoxide yields dibromo- ψ -cumenol, methyl acetate, and dibromo-*p*-hydroxy- ψ -cumyl methyl ether; when treated with hydrogen bromide in hot glacial acetic acid solution, the ether gives rise to a mixture of dibromo- ψ -cumenol and dibromo-*p*-hydroxy- ψ -cumyl bromide.

When the bromide, $\text{OAc}\cdot\text{C}_{17}\text{H}_{14}\text{OBr}_4\cdot\text{CH}_2\text{Br}$, is boiled with sodium acetate and glacial acetic acid or acetic anhydride, the corresponding *acetate*, $\text{OAc}\cdot\text{C}_{17}\text{H}_{14}\text{OBr}_4\cdot\text{CH}_2\cdot\text{OAc}$, melting at 204—205° is formed; but if acetic anhydride is employed and the time of heating increased, large quantities of the diacetyl derivative (m. p. 105—106°) of dibromo-*p*-hydroxy- ψ -cumyl alcohol are obtained.

W. A. D.

Hydrolysis of Benzonitrile. By CHARLES RABAUT (*Bull. Soc. Chim.*, 1899, [iii], 21, 1075—1076).—If 10 grams of benzonitrile are dissolved in 100 c.c. of alcohol and heated in a reflux apparatus for an hour with 6 grams of potassium hydroxide, 98 per cent. of the theoretical amount of benzamide is produced, but if only 1.12 or 0.56 gram of potassium hydroxide is used, the yield is reduced to 70 or 40 per cent. respectively. With concentrated potash, the product consists almost entirely of benzoic acid. No benzamide is formed when a dilute alcoholic solution of benzonitrile is heated for an hour in a sealed tube at 100°. N. L.

Isomeric Change of *o*-Amino- and *o*-Nitro-cinnamonitriles. By ROBERT PSCHORR and O. WOLFES (*Ber.*, 1899, 32, 3399—3405. Compare Abstr., 1899, i, 491).—*α*-*p*-Methoxyphenyl-*o*-nitrocinnamonitrile, $\text{NO}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{CH} : \text{C}(\text{CN}) \cdot \text{C}_6\text{H}_4 \cdot \text{OMe}$, crystallises from toluene or alcohol in minute, felted, yellow needles, melts at 162° (corr.), and sublimes without decomposition. 2-Amino-3-*p*-methoxyphenylquinoline, $\text{NH}_2 \cdot \text{C}_9\text{H}_5 \cdot \text{C}_6\text{H}_4 \cdot \text{OMe}$, prepared by reducing the preceding compound with tin and hydrochloric acid, crystallises from alcohol in colourless needles and melts at 151—152° (corr.); the salts are only slightly soluble, the *nitrate* melts at 207° (corr.), the *hydrochloride* at 226° (corr.), and the *sulphate* at 228° (corr.); the *platinichloride* forms yellow needles and decomposes at 240° (corr.), and the *picrate* forms minute, yellow needles and melts at 256° (corr.). 3-*p*-Methoxyphenyl-2-carbostyryl, $\text{OH} \cdot \text{C}_9\text{H}_5 \cdot \text{C}_6\text{H}_4 \cdot \text{OMe}$, prepared by the action of nitrous acid on the amino-compound, or by the action of acetic anhydride and sulphuric acid on *α*-paramethoxyphenyl-*o*-aminocinnamic acid, crystallises from alcohol in minute, colourless needles and melts at 259° (corr.).

Frost's *α*-phenyl-*o*-nitrocinnamonitrile (Abstr., 1889, 597), on reduction, gives 2-amino-3-phenylquinoline (Pschorr, Abstr., 1899, i, 491).

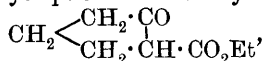
α-*p*-Nitrophenyl-*o*-acetaminocinnamonitrile can be converted directly by alcoholic hydrochloric acid into 2-amino-3-*p*-nitrophenylquinoline.

By heating with potassium hydroxide in dilute alcoholic solution, *α*-phenyl-*o*-nitrocinnamic nitrile is converted into hydrogen cyanide and *benzoylanthranilic acid*, which can also be prepared by the action of benzoyl chloride on anthranilic acid; it crystallises from alcohol in minute, colourless needles, melts at 181° (corr.), and gives a *monomethyl ester*, which crystallises from alcohol in colourless needles and melts at 101.5°. Similarly, *α*-*p*-methoxyphenyl-*o*-nitrocinnamic nitrile is converted by alcoholic potash into *anisylanthranilic acid*, $\text{OMe} \cdot \text{C}_6\text{H}_4 \cdot \text{CO} \cdot \text{NH} \cdot \text{C}_6\text{H}_4 \cdot \text{CO}_2\text{H}$, which crystallises from alcohol in scales and melts at 232° (corr.). T. M. L.

Tautomerism of *o*-Benzoylbenzoic Acid. By ALBIN HALLER and ALFRED GUYOT (*Compt. rend.*, 1899, 129, 1213—1216).—The formation of diphenylphthalide from *o*-benzoylbenzoic chloride points to the existence of a tautomeric form, $\text{C}_6\text{H}_4 \begin{smallmatrix} \text{CPhCl} \\ \diagup \quad \diagdown \\ \text{CO} \end{smallmatrix} \text{O}$, for this com-

pound. With a view of ascertaining whether methyl esters corresponding with the two forms of the acid are capable of existence, its esterification was carried out by five different methods. The *methyl* ester crystallising in colourless prisms and melting at 52° was obtained in every case. G. T. M.

Synthesis of Cyclopentane Derivatives by means of Ethyl Adipate. By LOUIS BOUVEAULT (*Bull. Soc. Chim.*, 1899, [iii], 21, 1019—1023).—Ethyl 2-cyclopentanonecarboxylate,



was shown by Dieckmann (Abstr., 1894, i, 173) to be formed by the action of sodium on ethyl adipate at 120° , and by a modification of the original process the author has obtained this compound in the pure state as a colourless, oily liquid, boiling at 113° under 22 mm. pressure, and having a sp. gr. 1.0976 at 0° . The sodium and potassium salts crystallise well and are not decomposed by water; the copper salt crystallises in thin, green plates melting at 183° , and dissolves in chloroform, yielding a violet solution. The *phenylhydrazone* is an oily liquid, whilst the *semicarbazone* crystallises in large, white needles melting at 143° . The sodium derivative of ethyl 2-cyclopentanonecarboxylate reacts with methyl iodide to form *methyl 1-methylcyclopentanonecarboxylate*,

$\text{CH}_2 \begin{array}{l} \swarrow \text{CH}_2 \cdot \text{CO} \\ \searrow \text{CH}_2 \cdot \text{CMe} \cdot \text{CO}_2\text{Et}' \end{array}$, which was obtained as a colourless oil, boiling at 108° under 22 mm. pressure, and having a sp. gr. 1.0529 at 0° . This forms a white, crystalline *semicarbazone* melting at 153° , and differs from its lower homologue in being insoluble in alkalis. When heated with concentrated hydrochloric acid, it yields 1-methylcyclopentanone, which Montemartini obtained by heating calcium adipate; this boils at 139° , and has a sp. gr. 0.7379 at 0° . It forms a liquid *oxime*, which boils at 103° under 22 mm. pressure, and yields a crystalline *benzoyl* derivative melting at 63.5° , and a crystalline *semicarbazone* which melts at 184° (Montemartini gives 171°). When boiled with alcoholic potash, ethyl methylcyclopentanonecarboxylate yields the potassium salt of α -methyladipic acid; if, however, a large excess of alkali is not employed, the potassium ethyl salt, $\text{CO}_2\text{K} \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{CHMe} \cdot \text{CO}_2\text{Et}$, is formed, which resists further hydrolysis. N. L.

Action of Potassium Hypobromite on Amides of Hydroxybenzoic Acids. By W. VAN DAM (*Rec. Trav. Chim.*, 1899, 18, 408—425).—By the action of potassium hypobromite on salicylamide, two dibromocarboxylaminophenols are obtained, one melting at above 270° and the other at 255° (McCoy, Abstr., 1899, i, 359, gave the melting point 250°), which is not identical with the compound obtained by Jacoby by the direct bromination of carboxylaminophenol; Jacoby's compound is found to melt at 255° , not at 243° as stated by him. The dibromocarboxylaminophenol melting at 255° , obtained by McCoy and by the author, forms a *methyl* derivative,



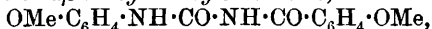
melting at 124° , an *acetyl* derivative, $\text{C}_6\text{H}_2\text{Br}_2 \begin{array}{c} \text{O} \\ \diagup \quad \diagdown \\ \text{NAc} \end{array} \text{CO}$, and a

barium compound, $C_6H_2Br_2 \begin{smallmatrix} O \\ \diagup \quad \diagdown \\ N_{ba} \end{smallmatrix} CO$, crystallising in white needles; it is readily soluble in acetone or alcohol, less so in ether or water, and from its solution in caustic potash solution the *potassium* derivative, $C_6H_2Br_2 \begin{smallmatrix} O \\ \diagup \quad \diagdown \\ N_K \end{smallmatrix} CO$, is deposited in white needles. Jacoby's compound does not form salts.

By the action of potassium hypobromite on *m*-hydroxybenzamide, *s-tribromo-m-hydroxybenzamide* $[CONH_2 : OH : Br_3 = 1 : 3 : 2 : 4 : 6]$ melting at 221° is obtained; if excess of alkali is present, tribromo-*m*-aminophenol melting at 117° is formed, the *triacetyl* compound of which, $OAc \cdot C_6HBr_3 \cdot NAc_2$, melts at 136° .

The action of barium hypobromite on *p*-hydroxybenzamide gives rise to dibromo-*p*-aminophenol melting at 191° .

Under the influence of bromine and sodium methoxide, anisoyl-amide condenses to $\alpha\beta$ -anisylanisoylcarbamide,



which melts at 222° .

The intramolecular change produced in the bromamides by the action of an alkali, by which they are converted into amides, is shown to be a reaction of the first order.

T. H. P.

Anisonitrile. By LOUIS HENRY (*Rec. Trav. Chim.*, 1899, 18, 466—467).—*p*-Methoxybenzonitrile and *p*-ethoxybenzonitrile described by Reinders and Ringer (*Abstr.*, 1899, i, 893) have already been prepared (Henry, *Ber.*, 1870, 2, 667; Pinner, *Abstr.*, 1891, 63).

T. H. P.

Resolution of Racemic Amino-acids into Optically Active Components. By EMIL FISCHER (*Ber.*, 1899, 32, 3638—3646. Compare *Abstr.*, 1899, i, 888).—A good yield of racemic benzoyl-tyrosine is obtained from *p*-hydroxy- α -benzoylaminocinnamic acid by a modification of Erlenmeyer and Halsey's method (*Abstr.*, 1898, i, 197). This compound is resolved into its active components by fractional crystallisation from aqueous solutions of its alkaloidal salts.

When brucine is employed, the first crop of crystals consists of the corresponding salt of benzoyl-*l*-tyrosine. *Benzoyl-l-tyrosine* crystallises in leaflets and melts at 165 — 166° , this temperature being 30° lower than the melting point of the racemic compound; $[\alpha]_D$ in an 8 per cent. alkaline solution at 20° is 19.25° , and with a 5 per cent. solution is 18.29° . *l*-Tyrosine is prepared by hydrolysing the benzoyl derivative with 10 per cent. hydrochloric acid; a more concentrated acid produces racemisation. The specific rotation in 20 per cent. hydrochloric acid at 20° is -8.64° , corresponding with the value -8.48° obtained by Schultze and Bosshard for the natural product; in 4 per cent. acid $[\alpha]_D$ is greater, that of the synthesised compound being -13.2° , whilst that of a specimen obtained from casein is -12.56° ; the latter result, however, does not agree with that of the above investigators, who found the rotation to be -15.6° .

Natural tyrosine, when rapidly heated, melts at 310 — 312° , whilst the racemic compound melts about 2° higher; the former separates in long, flexible crystals, the latter crystallises in stout needles.

Benzoyl-d-tyrosine is obtained from the racemic compound by the aid of cinchonine. The alkaloid salt separates somewhat slowly in flattened needles, and is obtained pure after two crystallisations. The *benzoyl* derivative melts at 165.5° ; in an alkaline solution $[\alpha]_D$ is -19.59° .

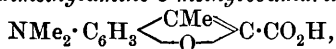
d-Tyrosine, dissolved in 21 per cent. hydrochloric acid, has $[\alpha]_D$ 8.64° . A base, supposed to be *d*-tyrosine, has been isolated by von Lippmann from the white shoots of the sugar beet in 25 per cent. hydrochloric acid; it gave $[\alpha]_D$ 6.85° .

The mother liquor from the brucine salt of *benzoyl-L-tyrosine* contains a mixture of racemic and dextro-salts; these are converted into the corresponding tyrosines, which are treated with hydrochloric acid, when the hydrochloride of the racemic base crystallises first; the *d*-tyrosine obtained from the mother liquor has a higher specific rotation than that obtained from the cinchonine salt. G. T. M.

Coumarins. I. Behaviour of Aminophenols with Ethyl Acetoacetate. By HANS VON PECHMANN (*Ber.*, 1899, 32, 3681—3690).—A summary and a discussion of previous results and of those enumerated in the following three abstracts. It is only *m*-aminophenols which condense with ethyl acetoacetate. R. H. P.

Coumarins. II. 7-Dimethylamino-4-methylcoumarin and Homologues. By HANS VON PECHMANN and MAX SCHAAL (*Ber.*, 1899, 32, 3690—3696).—*p*-Dimethylaminophenol and ethyl acetoacetate condense in the presence of zinc chloride to form 7-dimethylamino-4-methylcoumarin, which crystallises from dilute alcohol, with $3H_2O$, in the form of yellowish needles melting at 143° . On fusion with alkalis, it yields traces of 2-hydroxy-4-dimethylaminoacetophenone, which forms white leaflets melting at 120° , and a compound melting at 142° , which is probably bis-dimethylaminodihydrocoumarone, $C_{16}O_2H_{10}Me_2(NMe_2)_2$. Nitrous or nitric acid converts the 7-dimethylamino-4-methylcoumarin into a mononitro-derivative melting at 159° and a dinitro-derivative melting at 230° . Bromine in chloroform

solution yields the dibromide, $NMe_2 \cdot C_6H_3 \begin{smallmatrix} \text{CMeBr} \cdot \text{CHBr} \\ \diagdown \quad \diagup \\ \text{O} \quad \text{CO} \end{smallmatrix}$, which crystallises from glacial acetic acid in white needles melting and decomposing at 210° , and on boiling with alcohol is converted into 3-bromo-7-dimethylamino-4-methylcoumarin melting at 169° . On treatment of this monobromo-derivative with bromine, two isomeric dibromo-derivatives are obtained, one melting at 126° , the other at 184° . On dissolving the dibromide or the monobromo-derivative in alcoholic potash, 6-dimethylamino-3-methylcoumarilic acid,



is obtained; it forms grey needles melting and decomposing at 165° , and on heating yields 6-dimethylamino-3-methylcoumarone, which melts at 58° .

m-Dimethylaminophenol, ethyl acetoacetate, and alcohol condense in the presence of zinc chloride to form 7-dimethylamino-4-methyl-3-ethylcoumarin, which when crystallised from alcohol melts at 89° , but from benzene and light petroleum at 135° .

7-Diethylamino-4-methylcoumarin, obtained when *m*-diethylaminophenol is used, is an oil which yields a *tribromo*-derivative melting at 109°.

R. H. P.

Coumarins. III. 7-Amino-4-Methylcoumarin. By HANS VON PECHMANN AND OTTO SCHWARZ (*Ber.*, 1899, 32, 3696—3699).—*7-Amino-4-methylcoumarin*, prepared by the condensation of *m*-aminophenol and ethyl acetoacetate with zinc chloride, crystallises in fern-shaped forms, which sinter at 215° and melt at about 223°; it yields a *monoacetyl* derivative melting at 270°, and a *monobenzoyl* derivative melting at 249—250°. *7-Methylamino-4-methylcoumarin*, obtained in a similar manner from *m*-methylaminophenol, crystallises from dilute alcohol, with H₂O, in the form of small, yellow needles melting at 123°, and yields a *nitrosamine* melting at 189°. On heating *7-amino-4-methylcoumarin* with methyl iodide in a sealed tube at 100°, *4-methylcoumarin-7-trimethylammonium iodide*, $\text{NMe}_3\text{I} \cdot \text{C}_6\text{H}_3 \begin{smallmatrix} \text{CMe}:\text{CH} \\ \text{O} \text{---} \text{CO} \end{smallmatrix}$, is

obtained; it forms needles melting at 188°, and yields an insoluble platinichloride. The position of the amino-group in these coumarins is proved by the conversion of the aminocoumarin into *4-methylumbelliferone*.

R. H. P.

Coumarins. IV. Action of *m*-Aminophenol on Ethyl Acetoacetate. By HANS VON PECHMANN and OTTO SCHWARZ (*Ber.*, 1899, 32, 3699—3704).—In the condensation of *m*-aminophenol with ethyl acetoacetate by means of zinc chloride, in addition to *7-amino-4-methylcoumarin*, varying proportions of *7* (?) *-hydroxylepidone* (Besthorn and Byvanck, *Abstr.*, 1898, i, 450), *7* (?) *-hydroxy-2:4:4-trimethyl-3:4-dihydroquinoline*, and *4:6:6:8-tetramethyl-6:7-dihydroquinocoumarin* are formed.

7-Hydroxylepidone forms a *monoacetyl* derivative melting at 250—254°, and a *monobenzoyl* derivative melting at 288°.

7 (?) *-Hydroxy-2:4:4-trimethyl-3:4-dihydroquinoline* can be prepared by heating together molecular proportions of *m*-aminophenol and mesityl oxide; it forms a grey, amorphous powder without a definite melting point, and on treatment with ethyl acetoacetate and an alcoholic solution of zinc chloride yields *4:6:6:8-tetramethyl-6:7-dihydroquinocoumarin*, which forms yellow needles melting at 268°, and on treatment with bromine yields *5* (?) *:10 dibromo-4:6:6:8-tetramethyl-6:7-dihydroquinocoumarin dibromide*; this is obtained in the form of greenish-yellow needles which melt and decompose at 204°, and on treatment with alcoholic potash give *3:5* (?) *:10-tribromo-4:6:6:8-tetramethyl-6:7-dihydroquinocoumarin*, which forms small, yellow needles melting and decomposing at 191°. Either of the bromine compounds on continued boiling with alcoholic potash gives *4* (?) *:9-dibromo-3:5:5:7-tetramethyl-5:6-dihydrodibromoquinocoumarilic acid*, which melts and decomposes at 206°, and yields a *methyl ester* melting at 138°.

Molecular proportions of *m*-aminophenol and ethyl acetoacetate, when heated on the water-bath for 3 hours, give *ethyl m-hydroxyphenylaminocrotonate*, $\text{HO} \cdot \text{C}_6\text{H}_4 \cdot \text{NH} \cdot \text{CMe}:\text{CH} \cdot \text{CO}_2\text{Et}$, which at a temperature of 250—260° yields *4:7* (?) *-dihydroxy-2-methylquinoline*; this

crystallises, with H_2O , in the form of needles, which decompose at 300° without melting, and forms a *diacetyl* derivative melting at about 232° .
R. H. P.

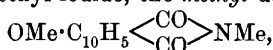
Derivatives of Naphthalic Acid. By FRITZ ANSELM and F. ZUCKMAYER (*Ber.*, 1899, 32, 3283—3296).—Concentrated sulphuric acid does not act on naphthalic acid (1:8-naphthalenedicarboxylic acid) at a high temperature, but sulphuric acid containing 25 per cent. of anhydride gives rise at 90 — 95° to the *monosulphonic* derivative, $\text{SO}_3\text{H}\cdot\text{C}_{10}\text{H}_5(\text{CO}_2\text{H})_2$, a white, deliquescent substance which melts at 198° , being converted into the anhydride; the *barium* and *calcium* salts (each with $1\text{H}_2\text{O}$) and the *sodium* and *potassium* salts (each with $1\frac{1}{2}\text{H}_2\text{O}$) were prepared.

On adding nitric acid (1 mol.) to naphthalic anhydride dissolved in sulphuric acid at 5° , the *mononitro*-derivative, $\text{NO}_2\cdot\text{C}_{10}\text{H}_5(\text{CO})_2\text{O}$, is obtained; it crystallises from glacial acetic acid in slightly brownish, lustrous leaflets and melts at 249° (compare Quincke, *Abstr.*, 1888, 843). On nitration with a mixture of sulphuric acid and 2 mols. of fuming nitric acid at 60° , naphthalic anhydride yields the *dinitro*-derivative, $\text{C}_{10}\text{H}_4(\text{NO}_2)_2(\text{CO})_2\text{O}$, which crystallises from toluene in yellowish-brown needles and melts at 214° . *Aminonaphthalic anhydride*, prepared by reducing the corresponding nitro-compound, is a yellow powder which melts above 300° and is nearly insoluble in all solvents, but the *acetyl* derivative, $\text{NHAc}\cdot\text{C}_{10}\text{H}_5(\text{CO})_2\text{O}$, crystallises from glacial acetic acid in yellowish-white needles; *diaminonaphthalic anhydride* was obtained only in the form of the *tin* salt. The *calcium* salt, $\text{Ca}[\text{SO}_3\cdot\text{C}_{10}\text{H}_4(\text{NO}_2)_2(\text{CO}_2)_2\text{Ca}]_2$, of nitrosulphonaphthalic acid, obtained by nitrating sulphonaphthalic acid, forms stout, yellow crystals.

Hydroxynaphthalic anhydride, $\text{OH}\cdot\text{C}_{10}\text{H}_5(\text{CO})_2\text{O}$, prepared by heating sodium sulphonaphthalate with solid potassium hydroxide initially at 180° , finally at 220° , crystallises from glacial acetic acid in bright yellow, silky needles ($+\frac{1}{3}\text{C}_2\text{H}_4\text{O}_2$), which on drying lose the acetic acid and become lustreless; the anhydride dissolves in alkalis to form initially a yellow salt by replacement of the hydroxylic hydrogen by the metal, but this immediately changes into a normal, colourless salt, owing to fission of the anhydride ring; the *potassium* salt, $\text{C}_{12}\text{H}_6\text{O}_5\text{K}_2$, forms beautiful, white needles. Since the hydroxy-anhydride unites with diazo-salts to form dyes, it appears probable that the hydroxyl group is not in the ortho- but in the para-position relatively to carboxyl; the hydroxy-anhydride can also be obtained from aminonaphthalic anhydride through the diazo-reaction. Like phthalic anhydride, hydroxynaphthalic anhydride furnishes cherry-red dyes of the naphthalein and rhodamine types. *Acetoxynaphthalic anhydride*, $\text{OAc}\cdot\text{C}_{10}\text{H}_5(\text{CO})_2\text{O}$, prepared by heating the hydroxy-anhydride with acetic anhydride, crystallises from ethyl acetate in white leaflets, and melts at 216° . *Hydroxynaphthalimide*, $\text{OH}\cdot\text{C}_{10}\text{H}_5\begin{smallmatrix} \text{CO} \\ \diagup \quad \diagdown \\ \text{CO} \end{smallmatrix} \text{NH}$,

prepared by heating the anhydride with alcoholic ammonia, crystallises from dilute acetic acid in yellowish-green needles, and shows no definite melting point; the *acetyl* derivative, $\text{C}_{14}\text{H}_9\text{O}_4\text{N}$, forms white

leaflets and melts at 278°. On heating the potassium salt of hydroxynaphthalimide with methyl iodide, the *methyl* derivative,

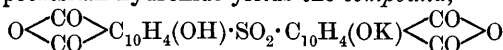


is formed, which separates from alcohol in yellowish-white, crystalline masses. *Hydroxynaphthalanilide*, $\text{OH} \cdot \text{C}_{10}\text{H}_5 \begin{array}{c} \diagup \text{CO} \diagdown \\ \diagdown \text{CO} \diagup \end{array} \text{NPh}$, prepared by heating the anhydride with aniline for 4 hours at 185°, crystallises from alcohol in yellowish-white, felted needles and melts above 300°; the *acetyl* derivative, $\text{OAc} \cdot \text{C}_{10}\text{H}_5 \begin{array}{c} \diagup \text{CO} \diagdown \\ \diagdown \text{CO} \diagup \end{array} \text{NPh}$, forms white needles and melts at 212°.

Hydroxynaphthaloxime, $\text{OH} \cdot \text{C}_{10}\text{H}_5 \begin{array}{c} \diagup \text{CO} \diagdown \\ \diagdown \text{C}(\text{N} \cdot \text{OH}) \diagup \end{array} \text{O}$, prepared by heating hydroxynaphthalic anhydride with alcoholic hydroxylamine hydrochloride and sodium acetate, crystallises from alcohol in lemon-yellow, sheaf-like aggregates of needles, and has no definite melting point; it yields intensely red salts with alkalis; the *potassium* salt, $\text{OH} \cdot \text{C}_{10}\text{H}_5 \begin{array}{c} \diagup \text{CO} \diagdown \\ \diagdown \text{C}(\text{N} \cdot \text{OK}) \diagup \end{array} \text{O}$, forms beautiful needles. *Diacetoxynaphthaloxime*, $\text{OAc} \cdot \text{C}_{10}\text{H}_5 \begin{array}{c} \diagup \text{CO} \diagdown \\ \diagdown \text{C}(\text{N} \cdot \text{OAc}) \diagup \end{array} \text{O}$, crystallises from alcohol in long, colourless needles and melts at 194°. On heating the potassium salt of the oxime with methyl iodide for 5 hours at 100°, the *dimethyl ether*, $\text{OMe} \cdot \text{C}_{10}\text{H}_5 \begin{array}{c} \diagup \text{CO} \diagdown \\ \diagdown \text{C}(\text{N} \cdot \text{OMe}) \diagup \end{array} \text{O}$, is obtained; it crystallises from alcohol in white, felted needles and melts at 191°. The *phenylhydrazone*, $\text{OH} \cdot \text{C}_{10}\text{H}_5 \begin{array}{c} \diagup \text{CO} \diagdown \\ \diagdown \text{C}(\text{N} \cdot \text{NHPh}) \diagup \end{array} \text{O}$, forms dark yellow needles and melts at 265°.

Methoxynaphthalic anhydride, prepared by heating the hydroxynaphthalic anhydride with methyl iodide and sodium methoxide, crystallises from ethyl acetate in yellowish-white needles and melts at 244°.

Hydroxysulphonaphthalic anhydride, prepared by the action of fuming sulphuric acid (25 per cent. SO_3) on hydroxynaphthalic anhydride at 115–120°, crystallises from water on adding alcohol in slightly yellow sheaves of needles; the *sodium* salt crystallises similarly, and on fusion with potassium hydroxide yields the *compound*,



or $\text{O} \begin{array}{c} \diagup \text{CO} \diagdown \\ \diagdown \text{CO} \diagup \end{array} \text{C}_{10}\text{H}_4(\text{SO}_3\text{K}) \cdot \text{O} \cdot \text{C}_{10}\text{H}_4(\text{OH}) \begin{array}{c} \diagup \text{CO} \diagdown \\ \diagdown \text{CO} \diagup \end{array} \text{O}$, which forms yellow crystals and is insoluble in most solvents. W. A. D.

Methyl Phloroglucinolcarboxylate. By JOSEF HERZIG and FRANZ WENZEL (*Ber.*, 1899, 32, 3541–3542. Compare Will and Albrecht, *Abstr.*, 1884, 1335).—*Methyl phloroglucinolcarboxylate*, $\text{C}_6\text{H}_2(\text{OH})_3 \cdot \text{CO}_2\text{Me}$, is readily obtained by the action of methyl iodide on the silver salt of the acid in the absence of any solvent. It crystallises from aqueous methyl alcohol in short, white needles melting at 166–168°, and is readily soluble in ether, alcohol, or

ethylic acetate. The *ethyl* ester may be obtained by a similar process, but does not crystallise readily. J. J. S.

Preparation of Hydroxystyrogallol. By FRANZ SLAMA (*Chem. Centr.*, 1899, ii, 967; from *Diss. Giessen.*, 1899, 29—34).—By the condensation of *p*-coumaric acid with gallic acid, *hydroxystyrogallol* or 2 : 3 : 6-*trihydroxyanthracoumarin*, $C_{16}H_8O_6$, is formed. The properties of this substance resemble those of Jacobsen and Julius' (Abstr., 1888, 56) and of Kostanecki's (Abstr., 1888, 291) compound. The more hydroxyl groups contained in the compound, the higher is the melting point, the more intense the colour, and the less the solubility. Hydroxystyrogallol is less soluble than styrogallol. The former dissolves in sulphuric acid, forming a red, and in potassium hydroxide or ammonia forming a green, solution. *Triacetoxystyrogallol*, $C_{16}H_5O_6(OAc)_3$, melts at about 250° in a vacuum.

E. W. W.

Solanthic Acid. By W. BRÄUTIGAM (*Chem. Centr.*, 1899, ii, 669; from *Pharm. Zeit.*, 44, 638).—*Solanthic acid*, $C_9H_{10}O_{10}$, prepared from the flowers and stems of *Helianthus annuus*, crystallises from water, melts at 144°, sublimes without decomposition, is soluble in alcohol, ether, or water, and forms crystalline salts. The acid is probably contained in the plant in the form of the calcium salt. E. W. W.

Metallic Derivatives of Salicylhydramide. By MARCEL DELEPINE (*Bull. Soc. Chim.*, 1899, [iii], 21, 943—945).—*Cupric methylsalicylimide*, $Cu(O \cdot C_6H_4 \cdot CH : NMe)_2$, obtained from the action of salicylaldehyde on cupric acetate and methylamine in alcoholic solution, or by adding a concentrated aqueous solution of cupric acetate to an alcoholic solution of methylsalicylimide, crystallises in long, dark green needles melting at 157°. *Cupric benzylsalicylimide*, $Cu(O \cdot C_6H_4 \cdot CH : N \cdot CH_2Ph)_2$, obtained in a similar manner from benzylsalicylimide, is an olive-green, crystalline substance which melts at 204°. A crystalline salt, having most probably the composition $Cu[O \cdot C_6H_4 \cdot CH(NMe_2)_2]_2$, is also yielded by dimethylamine.

The formation of these compounds leads the author to conclude that the compounds which Ettling (*Annalen*, 1840, 35, 241) obtained by the action of salicylhydramide on ammoniacal solutions of cupric acetate and ferric tartrate, are to be considered as derivatives of salicylimide of the type $Cu(O \cdot C_6H_4 \cdot CH : NR)_2$, and not as compounds of cuprammonium and ferrammonium respectively. N. L.

Preparation of Anisaldehyde. By HENRI LABBÉ (*Bull. Soc. Chim.*, 1899, [iii], 21, 1076—1077).—A yield of about 70 per cent. of anisaldehyde is obtained by the following modification of Cannizaro's original method. 1 part of anethole is mixed with 2 parts of anhydrous acetic acid and the liquid warmed, at first gently, and then more strongly, with $3\frac{1}{2}$ parts of nitric acid of 14° B. The insoluble oil which separates, together with a further portion which is obtained by saturating the aqueous liquid with sodium carbonate, is agitated with sodium hydrogen sulphite and the resulting crystalline mass

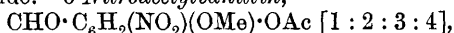
drained, washed with alcohol and ether, and treated in the usual manner. N. L.

Aldehyde-Musk. By ALBERT BAUR-THURGAU and AUGUST BISCHLER (*Ber.*, 1899, **32**, 3647—3648. Compare *Abstr.*, 1898, i, 523).—Butylxylylaldehyde is best prepared by heating the corresponding glyoxylic acid with *p*-toluidine and treating the product with sulphuric acid; it crystallises in large tablets melting at 60° and readily yields an *oxime*, which forms white plates melting at 97—98°. Nitric acid of 95 per cent. converts the aldehyde into a *mononitro*-compound, which crystallises in yellow, odourless plates melting at 66°. Nitric acid of 100 per cent., on the other hand, yields the *dinitro*-compound, $C_{13}H_{16}O_5N_2$ (aldehyde-musk, German Patent, No. 94019), crystallising in faintly yellow tablets melting at 112°. It yields two *oximes* of the same composition, $C_{13}H_{17}O_5N_3$; the one more readily soluble in alcohol is a microcrystalline powder melting at 138—139°, whilst the second *oxime* forms white plates melting at 171°. Aldehyde-musk readily forms condensation products with various compounds; the derivative, $C_{14}H_{17}O_6N_3$, obtained from nitromethane melts at 206°.

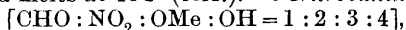
Acetic anhydride converts aldehyde-musk into a *diacetyl* derivative, $C_{17}H_{26}O_6N_2$, melting at 147°, which can also be obtained by converting butylxylylaldehyde into the *diacetyl* derivative melting at 87°, and treating this with nitric acid.

In the preparation of the aldehyde from butylxylylglyoxylic acid, a second compound is obtained, which has the composition $C_{26}H_{36}O$. A. H.

***o*-Nitrovanillin.** By ROBERT PSCHORR and C. SUMULEANU (*Ber.*, 1899, **32**, 3405—3413).—Acetylvanillin (Tiemann and Nagai, *Abstr.*, 1878, 579) can be advantageously prepared by shaking a solution of vanillin in the calculated amount of alkali with an ethereal solution of acetic anhydride. *o*-Nitroacetylvanillin,



prepared by dissolving acetylvanillin in well-cooled, concentrated nitric acid, crystallises from light petroleum in small, stout prisms, and melts at 85—87°; the *phenylhydrazone* crystallises in thin, reddish-brown plates and melts at 154° (corr.). *o*-Nitrovanillin,



crystallises from alcohol in minute needles and melts at 137° (corr.); the *phenylhydrazone* crystallises from acetic acid in brick-red prisms and melts at 161—162°. The *methyl ether* crystallises from dilute alcohol in long prisms, and gives a *phenylhydrazone*, which crystallises from acetic acid in saffron-yellow tablets and melts at 194° (corr.). *o*-Nitroveratric acid, $NO_2 \cdot C_6H_4(OMe)_2 \cdot CO_2H [= 2 : 3 : 4 : 1]$, was prepared by oxidation of *o*-nitrovanillin methyl ether, and found to be identical with Matsmoto's isonitroprotocatechuic acid dimethyl ether (*Abstr.*, 1879, 501); on reduction, it gives an *o*-aminoveratric acid identical with that prepared by Kühn (*Abstr.*, 1895, i, 367) from hemipinimide, thus establishing the constitution of Matsmoto's acid, and the position of the nitro-group in the present series of compounds. The structure of the amino-acid was further established by preparation

of the acetyl derivative, and by converting it, through the nitrile, into hemipinic acid.

o-Nitrovanillin methyl ether, $\text{CHO} \cdot \text{C}_6\text{H}_3(\text{OMe})_2 \cdot \text{NO}_2$ [1 : 3 : 4 : 6], was prepared by the action of cold nitric acid on vanillin methyl ether, and is isomeric with that prepared through the acetyl compound; it crystallises from alcohol in minute, yellow needles and melts at $132\text{--}133^\circ$ (corr.); the *phenylhydrazone* crystallises from acetic acid in glistening, reddish-brown, four-sided plates and melts at $216\text{--}218^\circ$ (corr.). The position of the nitro-group is shown by the fact that, like the isomeride previously described, the aldehyde gives the indigo-reaction, and is therefore a derivative of *o*-nitrobenzaldehyde. On oxidation, it gives a nitroveratric acid [$\text{CO}_2\text{H} : (\text{OMe})_2 : \text{NO}_2 = 1 : 3 : 4 : 6$] identical with that prepared by Tiemann and Matsmoto by nitration of veratric acid; the constitution of the latter is thus established.

T. M. L.

Condensation of Cyclic Ketones with Ethyl Succinate. By HANS STOBBE [AND RICHARD FISCHER] (*Ber.*, 1899, 32, 3354—3356. Compare *Abstr.*, 1899, i, 900).—When an ethereal solution of cyclopentanone and ethyl succinate is left in contact with sodium ethoxide (free from alcohol) for several weeks, and is then treated with water, the ethereal solution contains ethyl succinylsuccinate, together with small quantities of indifferent substances and the aqueous alkaline solution, a mixture of sodium salts of acid esters. After acidifying, hydrolysing with barium hydroxide, and fractional separation of the barium salt thus obtained, two *acids* have been obtained. One of these, $\text{C}_{14}\text{H}_{18}\text{O}_4$, crystallises from water, melts at 135° , and yields a sparingly soluble barium salt; it is formed by the elimination of two mols. of water from two mols. of the ketone and one of the ethyl ester. The second acid, $\text{C}_9\text{H}_{12}\text{O}_4$, crystallises from benzene, water, or ether, melts and decomposes at $205\text{--}209^\circ$, yields a readily soluble barium salt, and is produced from one mol. of the ketone and one of the ethyl ester.

J. J. S.

Methylcyclohexanone. By OTTO WALLACH (*Ber.*, 1899, 32, 3338—3341).—With reference to Klages' paper on methylcyclohexanone (this vol., i, 44), it is pointed out that the constitution of this substance has been previously determined in the author's laboratory by two independent methods. The first method is one of oxidation, whereby methylcyclohexanone is converted into β -methyladipic acid; the second consists in transforming the ketone into *m*-bromocresol.

The action of bromine on methylcyclohexanone has also been investigated; crystalline bromo-substitution products, which furnish cresol and bromocresol by removal of hydrogen, and compounds with tear-exciting odours have been obtained; the latter probably contain bromine in the side chain. The interaction between phosphorus pentachloride and methylcyclohexanone has also been studied, and the tetrahydrochlorotoluene produced has been characterised.

G. T. M.

Preparation of Tetrachloro- and Tetrabromo-*o*-quinones from the corresponding Tetrahaloid Guaiacols and Veratroles. By H. COUSIN (*Compt. rend.*, 1899, 129, 967—968).—When the tetra-

chloro- and tetrabromo-guaiacols or veratroles are subjected to Zincke's reaction, that is, oxidation with nitric acid, they give rise to the corresponding tetrahaloid *o*-quinones. The yields obtained are good when the guaiacol derivatives are used, but with the veratrole compounds they are poor, owing to fuming nitric acid being necessary for the oxidation.

Tetrachloro-*o*-quinone gives with benzene a compound, $C_6Cl_4O_2 + 3C_6H_6$, crystallising in large, red, elongated prisms, which rapidly lose the benzene in the air, leaving the tetrachloroquinone as a violet-red powder. T. H. P.

Stereochemistry of Quinoneoximes. By FRIEDRICH KEHRMANN (*Annalen*, 1899, 310, 89—111. Compare Abstr., 1899, i, 128).—[With O. KRÜGER].—3-*Chlorothymoquinone* [Me:O₂:Cl:Pr = 1:2:5:3:4], prepared by oxidising dichlorocarvacrol with chromic acid, is volatile in steam, and crystallises from alcohol in yellow leaflets melting at 41—42°; it separates from petroleum in crystals belonging to the rhombic system [*a*:*b*:*c* = 2.8449:1:1.1390]. The *oxime* decomposes at 158°, and separates from alcohol in crystals belonging to the monoclinic system [*a*:*b*:*c* = 1.5108:1:2.4862; β = 118°20′]. The *acetyl* and *benzoyl* derivatives of the oxime melt at 81—82° and 128—129° respectively.

3-Bromothymoquinone [Me:O₂:Br:Pr = 1:2:5:3:4] obtained from dibromocarvacrol by oxidation, is identical with the derivative obtained from bromocarvacrolsulphonic acid (compare Abstr., 1890, 367); the crystals from petroleum belong to the monoclinic system [*a*:*b*:*c* = 2.7130:1:1.1396; β = 91°51′]. The *oxime* decomposes at 157—158° and crystallises in prisms belonging to the monoclinic system [*a*:*b*:*c* = 2.6233:1:3.9232; β = 97°4′]. The *acetyl* and *benzoyl* derivatives of the oxime melt at 75—76° and 130—131° respectively.

3-Iodothymoquinone [Me:O₂:I:Pr = 1:2:5:3:4] has been already described, and crystallises in the monoclinic system [*a*:*b*:*c* = 2.5257:1:1.1396; β = 95°20′]. The *oxime* decomposes at 141—142°, and crystallises in the monoclinic system [*a*:*b*:*c* = 2.7031:1:3.7019; β = 96°2′]. The *acetyl* and *benzoyl* derivatives of the oxime melt at 99—100° and 144° respectively.

6-*Chlorothymoquinone* [Me:O₂:Pr:Cl = 1:2:5:4:6], prepared by oxidising dichlorothymol, crystallises from alcohol in golden-yellow prisms, and melts at 39—40°; it separates from petroleum in monoclinic crystals, having the axial ratios [*a*:*b*:*c* = 2.2533:1:2.5796; β = 95°22′]. The *oxime* crystallises from alcohol in pale yellow prisms belonging to the monoclinic system [*a*:*b*:*c* = 2.1203:1:0.8713; β = 99°36′], and decomposes at 152°. The *acetyl* derivative of the oxime forms rhombic crystals and melts at 76—77° [*a*:*b*:*c* = 0.5767:1:0.4777]. The *benzoyl* derivative separates in monoclinic crystals [*a*:*b*:*c* = 1.6793:1:1.1808; β = 97°6′], and melts at 126—127°.

6-Bromothymoquinone, which crystallises in the monoclinic system [*a*:*b*:*c* = 2.2284:1:2.5002; β = 94°11′] and melts at 46—47°, has been already described. The oxime also crystallises in the monoclinic system [*a*:*b*:*c* = 1.0699:1:0.8737; β = 103°38′]; the *acetyl* derivative

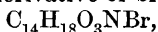
melts at 71—72°, and has the same axial ratios as the acetyl derivative of 6-chlorothymoquinoneoxime, and the *benzoyl* derivative, which melts at 119—120°, crystallises in the monoclinic system [$a:b:c = 1.6861:1:1.1873$; $\beta = 97^\circ 26'$].

6-Iodothymoquinone, which crystallises in the monoclinic system [$a:b:c = 2.0164:1:0.4834$; $\beta = 100^\circ 3'$] and melts at 61—62°, has been already described; the oxime is rhombic [$a:b:c = 0.9067:1:0.3905$]; the acetyl derivative melts at 67—68°, and has the same axial ratios as the acetyl derivative of 6-chlorothymoquinoneoxime, and the *benzoyl* derivative, which melts at 144°, crystallises in the rhombic system [$a:b:c = 0.6745:1:0.3799$].

[With M. SCHOEN].—*Chloronitrothymol* [$\text{Me}:\text{Cl}:\text{OH}:\text{Pr}:\text{NO}_2 = 1:2:3:4:6$], prepared by oxidising 6-chlorothymoquinoneoxime with nitric acid, crystallises from alcohol in pale yellow, lustrous needles, and melts at 116°; it is also produced when chlorine is passed into 6-nitrothymol dissolved in glacial acetic acid.

Bromonitrothymol [$\text{Me}:\text{Br}:\text{OH}:\text{Pr}:\text{NO}_2 = 1:2:3:4:6$], obtained on oxidising 6-bromothymoquinoneoxime, crystallises from alcohol in yellow prisms, and melts at 109°; it is also prepared by adding bromine to 6-nitrothymol dissolved in glacial acetic acid.

The *diacetyl* derivative of chloroaminocarvacrol, $\text{C}_{14}\text{H}_{18}\text{O}_3\text{NCl}$, obtained from 3-chlorothymoquinoneoxime by reduction with stannous chloride followed by acetylation, crystallises in long, lustrous needles, and melts at 175°; it is also produced when *p*-nitrocarvacrol [$\text{Me}:\text{OH}:\text{Pr}:\text{NO}_2 = 1:2:4:5$] is chlorinated, reduced, and finally acetylated. The *diacetyl* derivative of bromoaminocarvacrol,



prepared by analogous methods, crystallises in lustrous needles and melts at 157—158°.

M. O. F.

Halogen Derivatives of Anthragallol. By FRANZ SLAMA (*Chem. Centr.*, 1899, ii, 966—967; from *Diss. Giessen*, 1899, 1—26).—By the action of halogens on anthragallol, the halogen enters into the ring which contains the hydroxyl groups in a similar manner to the formation of nitro-derivatives (compare Bamberger and Böck, *Abstr.*, 1897, i, 576). When bromoanthragallol is melted, or oxidised by nitric acid, benzoic acid is formed, and when melted with potassium hydroxide at 200° it yields tetrahydroxyanthraquinone identical with Bayer and Co.'s compound (German Patent, 86968), hence the formula of the halogen derivative is $\text{C}_{14}\text{H}_4\text{Br}(\text{OH})_3\text{O}_2$ or 4-chloro-1:2:3-trihydroxyanthraquinone. When chlorine is passed into anthragallol suspended in glacial acetic acid, *chloroanthragallol* is formed; this crystallises in orange-red needles, melts at 220°, is soluble in alcohol, glacial acetic acid, or xylene, and forms a green solution in aqueous potassium hydroxide and a red in concentrated sulphuric acid. *Bromoanthragallol*, $\text{C}_{14}\text{H}_7\text{BrO}_5$, melts at 212°, decomposes when distilled in a vacuum, is oxidised by nitric acid, forming benzoic acid, and is decomposed by nitrous acid. Tetrahydroxyanthraquinone, $\text{C}_{14}\text{H}_4\text{O}_2(\text{OH})_4$, prepared by heating bromoanthragallol with potassium hydroxide and a little water at 206°, forms a sublimate consisting of green needles, and dissolves in sulphuric acid or aqueous potassium hydroxide, forming a red

solution. *Tetra-acetoxyanthraquinone*, $C_{13}H_4O_2(OAc)_4$, crystallises in yellow needles, melts at 205° , and dissolves in boiling aqueous potassium hydroxide, forming a violet-red solution, but is insoluble in the cold. *Chloroacetylchloroanthragallol*, prepared by the action of chloroacetyl chloride on chloroanthragallol, crystallises in silky, yellow needles and melts at $189-195^\circ$; *chloroacetyl bromoanthragallol* forms similar crystals and melts at $197-203^\circ$. The products obtained by the action of chloroacetyl chloride are not, however, homogeneous compounds. When the halogen compounds are boiled with acetic anhydride, triacetyl derivatives are obtained, hence these compounds contain three hydroxyl groups. *Chlorotriacetylanthragallol*, $C_{14}H_4ClO_2(OAc)_3$, crystallises in yellow needles, melts at 187° , and dissolves in boiling aqueous potassium hydroxide, forming a red solution, which quickly becomes green. *Bromotriacetylanthragallol*, $C_{14}H_4O_2Br(OAc)_3$, crystallises in yellow needles and melts at 178° . *Chlorotribenzoylanthragallol*, $C_{14}H_4O_2Cl(OBz)_3$, forms yellowish needles, melts at 209° , and dissolves in boiling aqueous potassium hydroxide, forming a green solution. *Bromotribenzoylanthragallol*, $C_{14}H_4O_2Br(OBz)_3$, forms yellow crystals, melts at 206° , is slightly soluble in glacial acetic acid or alcohol, but insoluble in cold aqueous potassium hydroxide. E. W. W.

Constitution of Camphor. By LOUIS BOUVEAULT (*Bull. Soc. Chim.*, 1899, [iii], 21, 1013-1019).—An account of the author's views on the constitution of camphor and its derivatives, and the researches which have led to their modification since 1892. Attempts to effect the synthesis of derivatives of camphoric acid have met with the same want of success as the experiments of Perkin (*Trans.*, 1899, 75, 909). Attempts to convert ethyl isoamylacetoacetate into ethyl isolaureonolate by the action of various dehydrating agents all failed. N. L.

Molecular Refraction and Dispersion and Specific Rotation of Alkyl Derivatives of Camphor. By ALBIN HALLER and PAUL TH. MÜLLER (*Compt. rend.*, 1899, 129, 1005-1008. Compare *Abstr.*, 1899, i, 770, ii, 622).—The molecular refraction and dispersion, and specific rotation of the following compounds have been determined: benzylidenecamphor, piperonylidenecamphor, cuminylcamphor, ethylsaligenylcamphor, *m*-methoxybenzylcamphor and *p*-methoxybenzylcamphor. The agreement between the found and calculated values (using Brühl's and Conrady's coefficients) is much closer than in the case of the compounds of camphor with aromatic aldehydes. This difference between the two values in the latter compounds is probably due to the double linking between the camphor and aldehyde groups, which is absent in the compounds enumerated above, hence the closer agreement. H. R. LE S.

Pulegone and Isopulegone. By CARL D. HARRIES and GEORG ROEDER (*Ber.*, 1899, 32, 3357-3373. Compare Beckmann and Pleissner, *Abstr.*, 1891, 936; Semmler, 1893, i, 130; Wallach, 1896, i, 309; Tiemann and Schmidt, 1897, i, 198).—Pulegonehydroxylamine (*Abstr.*, 1898, i, 573) forms an *oxalate*, $(C_{10}H_{19}O_2N)_2C_2O_4H_2$, which crystallises in prismatic needles melting and decomposing at $151-152^\circ$.

With nitrous acid, the hydroxylamine yields a white, crystalline mass, probably the nitrosamine, which is extremely unstable; it also reacts with hydriodic acid, yielding 8-aminomenthone (compare Beckmann and Pleissner), the *oxalate* of which has been prepared; so far, the authors have not succeeded in condensing this salt with different aldehydes (compare Fischer, Abstr., 1884, 53). *Bispulegone*, $C_{20}H_{34}O_2$, obtained by the action of aluminium amalgam on pulegone, crystallises in needles, melts at $118-119^\circ$, and is readily soluble in benzene, ether, or acetic acid; when sodium amalgam is used in acetic acid solution, considerable quantities of menthone and of menthol are also formed. When hydrobromopulegone is boiled with alcohol and lead hydroxide as recommended by Beckmann and Pleissner, the chief product is methylcyclohexanone (compare Wallach); the same product is formed when pulegone is boiled with ethyl alcohol and basic lead acetate, or when it is distilled with quinoline. When, however, the ketone is heated on the water-bath for half an hour with methyl alcohol and basic lead nitrate, a 70 per cent. yield of *α -isopulegone* is obtained; this may be separated from unaltered pulegone by treatment in ethereal solution with aluminium amalgam and subsequent distillation in steam, and finally purified by conversion into its oxime melting at $120-121^\circ$; the latter is identical with the oxime obtained by Tiemann and Schmidt. *α -Isopulegone* is a colourless oil distilling at $98-100^\circ$ under 13 mm. pressure, and has a sp. gr. 0.9192 at 19.5° , and a rotatory power $\alpha_D - 7.8'$, but when kept for some time in contact with dilute sulphuric acid, it becomes inactive; its semicarbazone, $C_{11}H_{19}ON_3$, crystallises from dilute alcohol in needles melting and decomposing at $173-174^\circ$. When an alcoholic solution of *α -isopulegone* is left for 24 hours in contact with baryta water, it is completely converted into ordinary dextrorotatory pulegone.

According to the authors, the isopulegone obtained by Tiemann and Schmidt's method yields a *semicarbazone* melting at 183° and an *oxime* melting at 143° ; they therefore term it *β -isopulegone*. According to recent experiments by Tiemann, a mixture of the α - and β -compounds is obtained by his method; these are probably the two inactive forms of the constitution $CHMe \begin{smallmatrix} \text{CH}_2-\text{CO} \\ \text{CH}_2 \cdot \text{CH}_2 \end{smallmatrix} > CH \cdot CMe \cdot CH_2$,

whereas pulegone is $CHMe \begin{smallmatrix} \text{CH}_2-\text{CO} \\ \text{CH}_2 \cdot \text{CH}_2 \end{smallmatrix} > C \cdot CMe_2$.

J. J. S.

Camphenylone. By EDMOND E. BLAISE and G. BLANC (*Compt. rend.*, 1899, 129, 886—889. Compare Abstr., 1899, i, 627, 629, 820).—If Jagelki's formula for camphoceenic acid, and Bredt's formula for isolauronic acid are correct, then the nitriles of these two acids on reduction should give one and the same amine. This, however, is not the case, as the following results show.

Camphenylone prepared by the action of nitric acid vapours on camphene at 0° , was purified by converting it into its *semicarbazone* melting at 224° , which, on treatment with hydrochloric acid, gives pure camphenylone, melting at 37° . The *oxime* readily sublimes and melts at $109-110^\circ$, and on dehydration with acetyl chloride, gives *camphoceanonitrile*, boiling at $220-230^\circ$, and an *iso-oxime* melting

at 165°. Camphoceanonitrile, on reduction with sodium and absolute alcohol, gives an unsaturated *base*, which boils at 204–205° and readily takes up carbon dioxide. The *hydrochloride* of this base is a white powder, which darkens at 195° and decomposes at 225°, and when treated with potassium cyanate gives a substituted *carbamide*, $C_9H_{15}\cdot NH\cdot CO\cdot NH_2$, crystallising in micaceous plates, which melt at 118° and are only slightly soluble in cold, but readily in hot, benzene. The *oxamide*, prepared by the action of ethyl oxalate on the base, forms needles which melt at 148°, and are very slightly soluble in alcohol; its *platinichloride* is a yellow powder insoluble in alcohol and in water. From the mother liquor of the hydrochloride of the above unsaturated base, the hydrochloride of an isomeric *base* was isolated; this boils at 195°, its *hydrochloride* melts at 175–176°, the *oxamide* and substituted *carbamide* at 106–107°, and the *picrate* at 178°.

The authors conclude that the trimethylcyclopentane group is not present in camphenylone and its derivatives. H. R. LE S.

Ethereal Oils. By SCHIMMEL AND CO. (*Chem. Centr.*, 1899, ii, 879–881; from *Geschäftsber.*, October, 1899).—There are two kinds of commercial oil of citronella, differing only slightly in physical properties and chemical composition. The ordinary oil “Lana Batu” contains less geraniol and citronellal than the better oil “Maha pangiri,” which is richer in compounds capable of forming acetyl derivatives. A sample of the former oil having a sp. gr. 0.908 at 15°, rotatory power $-9^{\circ}36'$, and containing 61.1 per cent. of geraniol and citronellal, was found not only to contain camphene, dipentene, and limonene, but also two sesquiterpenes; the one boils and decomposes at 260–270° under the ordinary pressure, and at 157° under 15 mm. pressure, has sp. gr. 0.8643 at 15°, rotatory power $+1^{\circ}28'$, and refractive index 1.51849 at 15°, whilst the other boils at 272–275° under the ordinary pressure, at 170–172° under 16 mm. pressure, has sp. gr. 0.912 at 15°, and rotatory power $+5^{\circ}50'$. The former terpene resinifies very easily, and this property explains the fact that, whilst many oils form clear solutions when dissolved in small quantities of 80 per cent. alcohol, they give turbid solutions when treated with four or more parts of the same alcohol.

The oil of citronella contained traces of linalool, about 1 per cent. of borneol and methyleugenol.

Another sample of citronella oil contained 33 per cent. of geraniol, 28 of citronellal, and 8 of methyleugenol.

The aqueous distillate obtained from oil of cumin contains methyl alcohol and furfuraldehyde. The yellowish colour of the former appears to depend on the presence of diacetyl; this is also the case with the methyl alcohol obtained from oil of cloves. The aqueous distillate of musk oil also contains furfuraldehyde.

About 9 per cent. of damascenine was extracted from nigella oil by shaking with tartaric acid and decomposing the tartrate with sodium carbonate; this compound has a blue fluorescence, solidifies in the cold, boils at 117° under 10 mm. pressure, and has a saponification number 277.4. From the alkaline liquid left after decomposing the

tartrate, a fluorescent acid, probably an amido-acid, was isolated; it crystallises from ether in prisms, is easily soluble in water, and forms a slightly soluble platinichloride. The presence of methoxy-groups in damascenine was confirmed.

Mustard oil always contains carbon disulphide, hence the determinations of sulphur do not exactly correspond with the amount of allylthiocarbimide present.

The fresh flowering plants and the roots of *Viola tricolor*, when distilled, yield 0.00859 per cent. of an ethereal oil, which consists mainly of methyl salicylate.

E. W. W.

Rhamninase and Xanthorhamnin. By CHARLES TANRET and GEORGES TANRET (*Bull. Soc. Chim.*, 1899, [iii], 21, 1073—1075. Compare this vol., i, 78).—Rhamninase is precipitated by alcohol from the cold water extract of the fruit of *Rhamnus infectoria* as a pasty mass containing 28—50 per cent. of solid matter; it is very soluble in water, and its activity does not diminish appreciably on keeping. The dry substance contains mineral salts (17 per cent.), substances coagulated by heat (53 per cent.), and galactan. A temperature of 70° is most favourable to the action of the enzyme, which is destroyed at 85°.

When xanthorhamnin is heated with water at 50°, a pale yellow, crystalline precipitate is gradually formed, quite different from that produced by the action of rhamninase. This substance is a new glucoside, which has a composition very similar to that of xanthorhamnin, but differs from it in not being acted on by rhamninase and in yielding a larger proportion of rhamnose on hydrolysis. The solution, from which the insoluble glucoside has been deposited, contains a substance, *xanthorhamnein*, which differs from xanthorhamnin in being more soluble and in having a higher rotatory power ($[\alpha]_D +5^\circ$ instead of $+3^\circ.75$). Schützenberger's observations on the existence of two modifications of xanthorhamnin are thus confirmed.

N. L.

Rhubarb and its Active Constituents. By ALEXANDER TSCHIRCH (*Arch. Pharm.*, 1899, 237, 632—637).—It is pointed out that Hesse (this vol., i, 40) is incorrectly informed as to the species of rhubarb cultivated in England for pharmaceutical purposes; also that chrysophanic acid has lately been shown to have a purgative action, although to a less degree than alochrysin, and still less than emodin.

C. F. B.

Colouring Matter of Digitalis. By L. ALPHONSE ADRIAN and AUGUSTE TRILLAT (*Compt. rend.*, 1899, 129, 889—890).—The substance $C_{16}H_{12}O_4$ was isolated from *Digitalis lutea* by a process analogous to that employed for the extraction of the yellow colouring matter from *Artemisia absinthium* (*Abstr.*, 1899, i, 301). It crystallises in beautiful, yellow needles, melts at 217—218°, and dissolves in ethyl alcohol, chloroform, or amyl alcohol; in alkalis, it is soluble, forming solutions of a beautiful red colour. Hydrochloric acid is without action on it, and it does not form a compound with phenylhydrazine, neither does it give a reducing sugar. When treated with hydrochloric acid or potash, neither catechol nor phloroglucinol is

produced, which shows that the substance is not identical with the digitoflavone of Fleischer. H. R. LE S.

Active Constituents of the Wallflower. By MORITZ REEB (*Chem. Centr.*, 1899, ii, 917—918; from *Arch. exp. Path. Pharm.*, 43, 130—148. Compare Abstr., 1899, i, 378).—The physiological action of cheiranthin resembles that of the digitalis compounds.

Cheirinine, $C_{18}H_{35}O_{17}N_3$, obtained from the alcoholic extract of the seeds of the wallflower, crystallises in small, colourless needles, melts at $73-74^\circ$, and is soluble in warm water, alcohol, ether, chloroform, or ethyl acetate. The aqueous solution is neutral and gives precipitates with the ordinary alkaloidal reagents. The physiological action of cheirinine resembles that of quinine.

The seeds also contain choline.

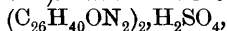
E. W. W.

Alkaloids of the Seeds of *Lupinus Angustifolius* and of *Lupinus Perennis*, var. *Polyphyllus*. By JÜRGEN CALLSEN (*Arch. Pharm.*, 1899, 237, 566—595. Compare Siebert, Soldaini, Davis, Berend, and Gerhard, Abstr., 1892, 223; 1893, i, 739; 1896, i, 193; 1897, i, 174, 645, 646).—No other alkaloid, in addition to *d*-lupanine, could be isolated from the seeds of blue and of perennial lupins; the yield of alkaloid is seven times as great in the case of the latter plant.

No new product, but only unchanged lupanine, could be isolated when lupanine was boiled with acetyl chloride, heated with fuming hydrochloric acid at $150-180^\circ$, heated with potassium permanganate and dilute sulphuric acid on the water-bath, allowed to remain with hydrogen peroxide at the ordinary temperature and in the dark, heated on the water-bath with water and yellow mercuric oxide, or with 10 per cent. nitric acid, treated in cold alcoholic solution with metallic sodium, heated at 200° with acetic anhydride or with dilute sulphuric acid, or on the water-bath with concentrated sulphuric acid, or at 150° with fuming hydriodic acid and amorphous phosphorus.

From the product of the action of bromine on lupanine hydrochloride in alcoholic solution, no alkaloid could be isolated (except unchanged lupanine) other than $C_8H_{15}ON$ (Davis; Soldaini, $C_8H_{13}ON$, *loc. cit.*). The *platinichloride*, $(C_8H_{15}ON)_2 \cdot H_2PtCl_6 + 1\frac{1}{2}H_2O$, decomposed at 200° ; the base is a tertiary one, for it does not unite with phenylthiocarbimide, and it forms a methiodide, the *platinichloride*, corresponding with which, $2(C_8H_{15}ONMe)_2PtCl_6 + 6H_2O$, decomposes just above 200° . C. F. B.

Alkaloids from the Salamander. By EDWIN S. FAUST (*Chem. Centr.*, 1899, ii, 718—719; from *Arch. exp. Path. Pharm.*, 43, 83—92. Compare Abstr., 1899, i, 380).—Samandarine sulphate,



which has been prepared in large quantities, crystallises either in small, anhydrous needles, usually arranged in small tufts or star-shaped groups, or occasionally in large, hydrated needles. It has a specific rotatory power $[\alpha]_D -53.69^\circ$, and gives a blue coloration when boiled with concentrated hydrochloric acid. When the platinichloride

is dried over sulphuric acid, it loses hydrogen chloride, and forms the compound $(C_{26}H_{40}ON_2)_2PtCl_4$. Experiments with dogs showed that doses of 0.0007—0.0009 gram per kilogram of body weight are fatal, the symptoms of samandarine poisoning being very similar to those of rabies.

The fire salamanders also contain another alkaloid, *samandaridine*, which appears to be present in larger quantities than samandarine. The *sulphate*, $(C_{20}H_{31}ON_2)_2SO_4$, crystallises in rhombic plates, is very slightly soluble in water or alcohol, is optically inactive, and has the same pharmacological action as samandarine sulphate, but to a less degree. When boiled with hydrochloric acid, it behaves like samandarine, and on distillation with zinc dust yields isoquinoline.

E. W. W.

Behaviour of Iodoform and Chloroform with Strychnine By PERRY F. TROWBRIDGE (*Arch. Pharm.*, 1899, 237, 622—625).—The compound $3C_{21}H_{22}O_2N_2 \cdot CHI_3$ (Lextreit, Abstr., 1881, 748) is formed even when 1 mol. of iodoform is allowed to react with 1 mol. of strychnine; the two substances were allowed to remain together in chloroform solution at the ordinary temperature for a day, and the compound then precipitated with ether. When it is boiled with alcohol, another compound, $2C_{21}H_{22}O_2N_2 \cdot CHI_3$, is obtained; this is also a reddish-brown, crystalline powder, which decomposes and melts at about 220°.

When a chloroform solution of strychnine is subjected to prolonged heating at 150°, a crystalline compound, $C_{21}H_{22}O_2N_2 \cdot HCl \cdot CHCl_3$, is obtained; this loses its chloroform partly at the ordinary temperature and entirely at 100°.

C. F. B.

Action of Methylene Iodide on Strychnine. By PERRY F. TROWBRIDGE (*Arch. Pharm.*, 1899, 237, 617—622).—When strychnine and methylene iodide are heated together in methyl alcoholic solution, or allowed to remain in chloroform solution at the ordinary temperature, a white, crystalline compound, $CH_2I \cdot C_{21}H_{22}O_2N_2I$, is obtained; this melts at 212°, and readily exchanges one of its iodine atoms for chlorine, &c. The corresponding *chloride*, $CH_2I \cdot C_{21}H_{22}O_2N_2Cl$, *aurichloride*, *platinichloride*, *mercurichlorides*, $CH_2I \cdot C_{21}H_{22}O_2N_2Cl \cdot HgCl_2$, and with $1\frac{1}{2}HgCl_2$, *bromide*, *hydrogen sulphate*, *hydrogen chromate*, and *nitrate* were prepared and analysed.

C. F. B.

Action of Iodine on Piperidine, Tetrahydroquinoline, and Tetrahydroisoquinoline. By ERNST SCHMIDT (*Arch. Pharm.*, 1899, 237, 561—565).—When tetrahydroquinoline is heated with iodine and alcohol in a closed vessel in the steam-bath, it is oxidised to quinoline. Tetrahydroisoquinoline, however, yields but little isoquinoline under similar circumstances, and piperidine does not yield pyridine.

C. F. B.

6-Aminoquinoline and its Derivatives. By CHR. A. KNUEPPEL (*Annalen*, 1899, 310, 75—88. Compare Abstr., 1896, i, 391).—6-Aminoquinoline, prepared by reducing 6-nitroquinoline in alcohol with iron borings, yields the *hydrochloride* in golden-yellow needles

melting at 109° ; the dihydrochloride is insoluble in hot alcohol and melts at 250° .

Thionyl-6-aminoquinoline, $C_9NH_6 \cdot N \cdot SO$, crystallises in small, yellow needles, and melts at $64-65^{\circ}$; it is gradually decomposed by hot water, yielding sulphur dioxide; *6-aminoquinolinethionamic acid*, $C_9NH_6 \cdot NH \cdot SO_2H$, melts at 124° .

6-Quinylurethane, $C_9NH_6 \cdot NH \cdot CO_2Et$, crystallises from hot alcohol in brownish plates, and melts at 168° ; the *hydrochloride* forms white needles.

6-Acetylaminquinoline, $C_9NH_6 \cdot NHAc$, crystallises from hot water in white needles melting at 138° , and the *hydrochloride* also forms needles; the *salicylate*, *tartrate*, and *methiodide* melt at 140° , 226° , and 268° respectively.

6-Benzoylaminquinoline, $C_9NH_6 \cdot NHBz$, crystallises in yellowish needles and melts at 169° ; the *sulphate*, *hydrochloride*, and *nitrate* are well crystallised substances.

6-Quinolinehydrazine, $C_9NH_6 \cdot NH \cdot NH_2$, has not been obtained in crystalline form, but derivatives are easily obtained. The *benzylidene* compound separates from water in long, reddish-yellow needles, and from alcohol in deep red cubes melting at 203° ; the *semicarbazide* derivative melts at 234° , and the *pyruvic hydrazone* crystallises in orange-red needles melting at 201° .

6-Azoquinoline, $N_2(C_9NH_6)_2$, a bye-product in the preparation of 6-aminoquinoline, crystallises in lustrous, orange-red needles and melts at 248° . *6-Azoxydiquinoline*, $C_{18}H_{10}ON_4$, prepared by heating 6-nitroquinoline with sodium methoxide in methyl alcohol, crystallises from alcohol in dark violet needles and does not melt below 280° ; the solution in sodium hydroxide is deep green. *6-Azodiquinoline*, $C_{18}H_{10}N_4$, obtained when the foregoing substance is distilled with iron borings in an atmosphere of hydrogen, crystallises from xylene in yellow needles, infusible below 280° .

Dimethylaminobenzene-6-azoquinoline, $C_9NH_6 \cdot N \cdot N \cdot C_6H_4 \cdot NMe_2$, prepared from diazotised 6-aminoquinoline and dimethylaniline, crystallises from alcohol in lustrous, steel-blue needles. *Benzene-6-diazo-aminoquinoline*, $C_9NH_6 \cdot NH \cdot N \cdot NPh$, formed on adding diazobenzene chloride to aminoquinoline, crystallises in long, orange-yellow needles, melting at 142 ; the *hydrochloride* is crystalline, and the *methiodide* melts at 220° .
M. O. F.

4-Hydroxycarbostyryl from Anthranilic Acid. By HUGO ERDMANN (*Ber.*, 1899, 32, 3570—3573. Compare Baeyer and Bloem, *Abstr.*, 1883, 196, and Camps, this vol., i, 115).—4-Hydroxycarbostyryl is obtained when methyl anthranilate (*Abstr.*, 1899, i, 621) is heated on the water-bath with ethyl acetate and metallic sodium for some three hours. The product is treated with ice-cold acetic acid and then shaken with water and ether, when the carbostyryl begins to separate. The ethereal filtrate contains *methyl diacetyl anthranilate*, $NAc_2 \cdot C_6H_4 \cdot CO_2Me$, together with more hydroxycarbostyryl. This diacetyl derivative crystallises in glistening prisms melting at 180° , has a burning taste, dissolves in boiling alkalis, and is decomposed by dilute mineral acids.

Acetylanthranilic acid melts at 185° , and its methyl ester at 101° ; acetylsalicylic acid melts at 132° , and its methyl and phenyl esters at 49° and 98° respectively.

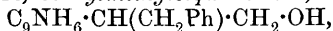
J. J. S.

Action of Aldehydes on Quinoline Derivatives containing a Methyl or Methylene Group in Position 2 or 4. By WILHELM KOENIGS (*Ber.*, 1899, **32**, 3599—3613).—When benzaldehyde is heated with quinaldine (2 mols.) in presence of zinc chloride at 150 — 160° , a small quantity of benzylidenequinaldine (Doebner and von Miller, *Abstr.*, 1885, 1080) is formed together with a larger proportion of *benzylidenediquinaldine*, $\text{CHPh}(\text{CH}_2\cdot\text{C}_9\text{NH}_6)_2$, the *hydrochloride* of which crystallises from absolute alcohol containing hydrochloric acid in beautiful, colourless plates*; the *nitrate* and *sulphate* form colourless crystals, whilst the *platinichloride*, with $3\text{H}_2\text{O}$, consists of yellow prisms and melts and decomposes at 240° . The *base* is a colourless, soft resin and cannot be obtained crystalline. When heated with benzaldehyde in presence of zinc chloride for 7—8 hours at 160 — 170° , it yields a large quantity of resin, together with a small amount of benzylidenequinaldine, the expected tetramethylene derivative, $\text{C}_9\text{NH}_6\cdot\text{CH}\left\langle\begin{smallmatrix}\text{CHPh} \\ \text{CHPh}\end{smallmatrix}\right\rangle\text{CH}\cdot\text{C}_9\text{NH}_6$, apparently not being formed.

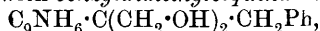
Benzylidenedilepidine, prepared in the same manner as the corresponding quinaldine derivative, crystallises from alcohol in colourless prisms and melts and decomposes indefinitely between 110° and 127° ; the *hydrochloride*, with $2\text{H}_2\text{O}$, crystallises in concentric aggregates of needles, whilst the *platinichloride*, with $6\text{H}_2\text{O}$, forms a flocculent mass of yellow needles.

Benzylmethylollepidine, $\text{C}_9\text{NH}_6\cdot\text{CH}(\text{CH}_2\text{Ph})\cdot\text{CH}_2\cdot\text{OH}$, prepared by heating benzyllepidine with 40 per cent. aqueous formaldehyde in a sealed tube for 45 hours at 100° , crystallises from benzene in colourless, pointed prisms, and melts at 150° ; the *platinichloride* forms a yellowish, crystalline mass of leaflets. The base is not further acted on by heating with formaldehyde for 9 hours at 140° , and is not changed by similar treatment with benzaldehyde for 10 hours at 180 — 200° .

When benzylquinaldine is heated with 40 per cent. aqueous formaldehyde for 38 hours, *benzylmethylolquinaldine*,



crystallising from ether in prisms or plates and melting at 113 — 114° , is formed together with *benzyltrimethylolquinaldine*,

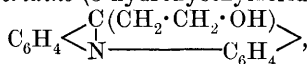


which crystallises from alcohol in colourless prisms, melts at 141 — 142° , and yields a crystalline *hydrochloride* which sinters at 185° and melts and decomposes at 190° ; the bases were separated by means of their *oxalates*. Chloral condenses with benzylquinaldine in the same manner as formaldehyde, a crystalline *compound* melting at 173° being obtained. An attempt to obtain benzylquinaldine by the interaction of benzyl alcohol with quinaldine gave no result. Benzylidenequinaldine does not react with formaldehyde.

* The original gives 156° and also 218° as the melting point of benzylidenediquinaldine hydrochloride.

Since lepidine combines with only two mols. of formaldehyde, whereas quinaldine combines with three (Abstr., 1898, i, 74 and 389), and benzyllepidine with one, although benzylquinaldine unites with two, it would appear that the benzene nucleus in the ortho-position to the methyl radicle of lepidine exercises a stereochemical, inhibiting effect; this hypothesis is, however, weakened by the fact that 5-methylacridine, which contains two benzene nuclei adjacent to the active methyl radicle, condenses with 2 mols. of formaldehyde but 5-ethylacridine, in which one of the active hydrogen atoms is replaced by a methyl radicle with only one; acridine itself does not react with formaldehyde, yet 3-methyl-2-ethylquinoline condenses with one mol. of formaldehyde, and thus behaves like benzyllepidine.

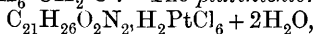
Methylol-5-methylacridine (5-hydroxyethylacridine),



the principal product obtained on heating 5-methylacridine with dilute alcoholic formaldehyde, is a yellow, amorphous substance, which melts at 115—125° and yields a *hydrochloride* crystallising in yellow needles; with it there is formed a small quantity of *dimethylol-5-methylacridine*, $\text{C}_{16}\text{H}_{15}\text{O}_2\text{N}$, which crystallises from alcohol in sulphur-yellow needles and melts at 194°. *Methylol-5-ethylacridine*,

$\text{C}_6\text{H}_4 \begin{array}{c} \diagup \text{C}(\text{CHMe} \cdot \text{CH}_2 \cdot \text{OH}) \\ \diagdown \text{N} \end{array} \text{C}_6\text{H}_4$, obtained similarly from 5-ethylacridine, separates from ethyl acetate in stout, yellow, lustrous crystals and melts at 183°; the *aurichloride* forms yellow crystals, and the *platinichloride* orange-yellow needles which melt and decompose at 225°.

Although cinchonine and conchinine do not interact with formaldehyde at 130—140°, the corresponding deoxy-bases condense with 1 mol. of the aldehyde at 100°; it thus appears that the alkaloids contain the lepidine complex $\text{C}_9\text{NH}_6 \cdot \text{CH}(\text{OH}) \cdot \text{C}$, and the deoxy-bases the group $\text{C}_9\text{NH}_6 \cdot \text{CH}_2 \cdot \text{C}$. The *platinichloride*,



of *methyloldeoxyconchinine* darkens at 215°, but does not melt at 270°; the *base* is amorphous, and the other salts, with the exception of the *picate*, are similar in nature. *Methyloldeoxycinchonine*, and its *platinichloride*, $\text{C}_{20}\text{H}_{24}\text{ON}, \text{H}_2\text{PtCl}_6 + 2\text{H}_2\text{O}$, resemble the corresponding cinchonine derivatives.

Papaverine interacts with formaldehyde at 100°, with elimination of $1\text{H}_2\text{O}$, to form *methylenepapaverine*, $\text{C}_{21}\text{H}_{21}\text{O}_4\text{N}$, which crystallises from alcohol, on adding ether, in colourless aggregates of needles, melts at 155—156°, and yields a yellow, crystalline *platinichloride* melting and decomposing between 150° and 180°; the *hydrochloride* sinters at 105°, melts at 110°, and decomposes at 130—140°; the *hydrobromide* melts at 110° and decomposes at 120°, whilst the *picate* sinters at 100° and melts at 115°.

W. A. D.

Amino-derivatives of α -Phenylbenzothiazole. By OTTO KYM (*Ber.*, 1899, 32, 3532—3538. Compare Abstr., 1899, i, 647 and 943).—*Dinitrophenyl thiobenzoate*, $\text{C}_6\text{H}_3(\text{NO}_2)_2 \cdot \text{S} \cdot \text{COPh}$ [$\text{S} : \text{NO}_2 : \text{NO}_2 = 1:2:4$], can be prepared by the Schotten-Baumann method from dinitro-

phenyl mercaptan and benzoyl chloride, but more readily by mixing alcoholic solutions of chlorodinitrobenzene and potassium thiobenzoate; it crystallises from dilute acetone in long, glistening, yellow needles, melts at 111—112°, and is readily hydrolysed to dinitrophenyl mercaptan and benzoic acid; tetranitrodiphenyl sulphide is also produced, especially when the alcoholic solutions are heated. 1-Phenyl-4-amino-benzothiazole, $\text{NH}_2 \cdot \text{C}_6\text{H}_3 \langle \text{S} \rangle \text{CPh}$, prepared by reducing the preceding compound by Nietzki's method (Abstr., 1897, i, 277), melts at 201—202°, forms yellowish-green crystals, and gives yellow solutions with a greenish fluorescence, but forms a white, sparingly soluble sulphate. The acetyl derivative crystallises from dilute alcohol in glistening, white needles, melts at 192—193°, and shows a slight violet fluorescence in solution.

p-Nitrothiobenzoic acid, $\text{NO}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{CO} \cdot \text{SH}$, crystallises from dilute hydrochloric acid in long, slender, yellowish-white needles and melts at 90—95°; the disulphide crystallises from dilute acetone in large, glistening, yellowish-white leaflets, melts at 182—183°, and is reconverted into dinitrothiobenzoic acid by warming with alcoholic potash; the dinitrophenyl ester crystallises from acetone or acetic acid in glistening, yellowish-white flakes, melts at 139—140°, and is hydrolysed by aqueous potash to dinitrophenylmercaptan and p-nitrobenzoic acid. 1-p-Aminophenyl-4-aminobenzothiazole, $\text{NH}_2 \cdot \text{C}_6\text{H}_3 \langle \text{S} \rangle \text{C} \cdot \text{C}_6\text{H}_4 \cdot \text{NH}_2$, prepared by reducing the trinitro-ester, crystallises from dilute acetone or alcohol in long, yellow, glistening needles, melts at 237—238°, and closely resembles the corresponding oxazole, but does not form an insoluble hydrochloride, and shows a yellowish-green fluorescence in solution; the acetyl derivative crystallises from dilute alcohol in reddish-white, glistening needles, melts at 272—273°, and shows an intense reddish-violet fluorescence in solution. T. M. L.

Methyl-o-anisidine, Methyl-o-aminophenol and their Oxidation Products (6-Methylphenoxazine-2:3-quinone). By EMIL DIEPOLDER (*Ber.*, 1899, 32, 3514—3528).—When o-nitroanisole is reduced with tin and hydrochloric acid, a mixture of o-anisidine and chloroanisidine [$\text{OMe} : \text{NH}_2 : \text{Cl} = 1 : 2 : 5$] is produced (Herold, Abstr., 1882, 1287; Reverdin and Eckard, this vol., i, 28), which is best separated by conversion into the formyl derivatives. Formyl-o-anisidine crystallises from dilute alcohol in long, colourless needles, melts at 83·5°, and dissolves in hot water and organic solvents. 5-Chloro-2-formyl-aminoanisole crystallises from alcohol in thin, colourless tablets, melts at 177—178°, is less soluble than the preceding compound, and is hydrolysed by boiling sodium hydroxide solution. Methyl-o-anisidine, prepared by methylating formyl-o-anisidine, boils at 141—143° under 46—47 mm. pressure, and solidifies to long prisms which melt at 33—33·5°.

Benzenesulphon-o-anisidine crystallises from alcohol and from hot water, and melts at 89°; the sodium derivative is readily soluble in water, but is precipitated in white needles by strong sodium hydroxide. Benzenesulphonmethyl-o-anisidine crystallises from a mixture of ether

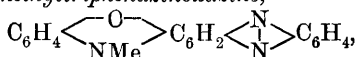
and light petroleum in well formed tablets and prisms, and melts at 60°.

o-Methoxyphenylglycine, when purified, melts at 153°, and crystallises in white, flat needles (compare Vater, Abstr., 1884, 1144).

Methyl-o-nitrosoaminophenol, $\text{OH} \cdot \text{C}_6\text{H}_4 \cdot \text{NMe} \cdot \text{NO}$, crystallises from dilute alcohol in needles, darkens at 100°, and decomposes at 121°, dissolves readily in hot water and dilute sodium hydroxide solution, and gives Liebermann's reaction, but could not be converted into a paranitroso-compound.

5-Methylphenoxazine-2:3-quinone, $\text{C}_6\text{H}_4 \begin{smallmatrix} \text{O} \\ \text{NMe} \end{smallmatrix} \begin{smallmatrix} \text{C}:\text{CH}:\text{CO} \\ \text{C}:\text{CH}:\text{CO} \end{smallmatrix}$, prepared by oxidising methyl-*o*-aminophenol with potassium ferricyanide, melts with decomposition at 212—213°, separates from chloroform in dark-red crystals with a green shimmer, and gives a greenish-blue coloration with stannous chloride; its constitution is established by hydrolysis with sodium hydroxide to methyl-*o*-aminophenol and a dihydroxy-*o*-quinone, which passes into Nietzki and Schmidt's *p*-dihydroxy-*p*-quinone; when the latter is condensed with methyl-*o*-aminophenol, a small amount of the phenoxazinequinone appears to be reproduced.

5-Methylphenoxazine-2:3-quinonemonoxime is a reddish-brown, microcrystalline powder which dissolves in dilute sodium hydroxide solution, but is hydrolysed by heating with mineral acids; it darkens at 185° and melts, with decomposition, at 200—201°; the dioxime could not be isolated in a pure state. With *o*-aminophenol, the quinone gives Seidel's triphenodioxazine (Abstr., 1890, 490). With *o*-phenylenediamine, it gives *N*-methyltriphenazinoxazine,



or, possibly, $\text{C}_6\text{H}_4 \begin{smallmatrix} \text{O} \\ \text{NMe} \end{smallmatrix} \text{C}_6\text{H}_2 \begin{smallmatrix} \text{N} \\ \text{N} \end{smallmatrix} \text{C}_6\text{H}_4$, which crystallises from a mixture of benzene and absolute alcohol in orange-yellow needles, melts at 250°, sublimes with partial decomposition at higher temperatures, dissolves in organic solvents, giving yellow, fluorescent solutions, and in sulphuric acid with a blue coloration. With *o*-aminodiphenylamine and hydrochloric acid, the quinone gives *N*-methyltriphenoxazinephenylazonium chloride, $\text{C}_6\text{H}_4 \begin{smallmatrix} \text{O} \\ \text{NMe} \end{smallmatrix} \text{C}_6\text{H}_2 \begin{smallmatrix} \text{N} \\ \text{NPhCl} \end{smallmatrix} \text{C}_6\text{H}_4$, or $\text{C}_6\text{H}_4 \begin{smallmatrix} \text{NMe} \\ \text{O} \end{smallmatrix} \text{C}_6\text{H}_2 \begin{smallmatrix} \text{N} \\ \text{NPhCl} \end{smallmatrix} \text{C}_6\text{H}_4$ (compare Witt, Abstr., 1887, 729), which separates in small, bronzy needles and dissolves in water or alcohol to violet-blue solutions; the azonium base dissolves in benzene to a reddish, fluorescent solution; the *platinichloride* is a blue, microcrystalline precipitate soluble in hot water. T. M. L.

Action of Nitrous Acid on the Leuco-base, $\text{C}_{13}\text{H}_{24}\text{N}_2$. By AUGUSTE TRILLAT (*Compt. rend.*, 1899, 129, 1242—1243).—Unsymmetrical tetramethyldiaminodiphenylethane (Abstr., 1899, i, 615), when treated with sodium nitrite in cold hydrochloric acid solution, yields *p*-nitrodimethylaniline. A similar result is obtained with the leuco-bases derived from methane. G. T. M.

Constitution of Metallic Salipyrynes (Metallic Antipyryne-salicylates). By EDOUARD BOURGEOIS (*Rec. Trav. Chim.*, 1899, 18, 451—456).—Objections are taken to Schuyten's views (this vol., i, 57) as to the structure of metallic salipyrynes. T. H. P.

History of Diazonium Salts. By EUGEN BAMBERGER (*Ber.*, 1899, 32, 3633—3635. Compare *Abstr.*, 1899, ii, 685 and 750).—A reply to Hantzsch (this vol., i, 126). The diazonium perbromide constitution, $\text{NPhBr}_3\text{:N}$, for the perbromides of diazonium salts was only suggested by Hantzsch after the ammonium formula for the radicle PhN_2 had been substantiated. The solubility of the diazonium carbonates and the physico-chemical evidence as to the nature of the ion of diazonium salts, merely confirm the author's views on the ammonium theory of the constitution of these compounds. G. T. M.

Action of Aromatic Nitroso-derivatives on *as*-Alkyl Aromatic Hydrazines. By EUGEN BAMBERGER and ARMAND STIEGELMANN (*Ber.*, 1899, 32, 3554—3560. Compare *Abstr.*, 1896, i, 222).—The production of diazohydroxyaminobenzene, $\text{NPh:N}\cdot\text{NPh}\cdot\text{OH}$, from nitrosobenzene and phenylhydrazine, is probably preceded by the direct addition of the constituents to form a compound, $\text{OH}\cdot\text{NPh}\cdot\text{NH}\cdot\text{NPh}$, which, by the loss of two atoms of hydrogen, yields diazohydroxyaminobenzene. This conclusion is supported by the behaviour of nitrosobenzene towards unsymmetrical phenylmethylhydrazine. When the two are brought together, the chief product is benzeneazomethylaniline oxide, $\text{O:NPh:N}\cdot\text{NMePh}$ or $\text{O} < \begin{smallmatrix} \text{NPh} \\ | \\ \text{N}\cdot\text{NMePh} \end{smallmatrix}$, and it is probably formed by the loss of two atoms of hydrogen from the direct additive compound $\text{OH}\cdot\text{NPh}\cdot\text{NH}\cdot\text{NPh}$. A secondary product formed in the same reaction is diazomethylaminobenzene (benzeneazomethylanilide), $\text{NPh:N}\cdot\text{NMePh}$, formed by the elimination of water from the additive compound. Other bye-products are also formed, mainly by the action of the hydrogen from the intermediate additive compound. The azoamine oxides, as a group, crystallise readily in yellow-coloured crystals which are very stable. They differ from azoamines (*Abstr.*, 1898, i, 20) in that they give no coloration with naphthylamine acetate, but readily give Liebermann's reaction. When reduced, they yield diazoamines, primary and secondary aromatic amines, azo-, azoxy-, and hydrazo-compounds, hydrazine, and ammonia.

Benzeneazomethylaniline oxide crystallises in glistening, sulphur-yellow needles melting at 72° , and is readily soluble in most organic solvents with the exception of light petroleum. When reduced, it yields diazomethylaminobenzene, aniline, methylaniline, ammonia, and unsymmetrical phenylmethylhydrazine.

Benzeneazodiphenylamine oxide, $\text{O:NPh:N}\cdot\text{NPh}_2$, obtained together with phenylhydroxylamine, and probably diphenylamine, by the action of nitrosobenzene on unsymmetrical diphenylhydrazine, crystallises in sulphur-yellow needles, melts at $128\cdot5$ — 129° , and is soluble in most organic solvents, including hot light petroleum.

p-Bromobenzeneazomethylaniline oxide, $\text{C}_6\text{H}_4\text{Br}\cdot\text{NO:N}\cdot\text{NMePh}$, crystallises in brass-yellow plates melting at 77 — 78° , and is only sparingly

soluble in cold light petroleum. *p*-Bromobenzeneazodiphenylamine oxide is formed, together with *p*-bromophenylhydroxylamine and *p*-dibromoazoxybenzene, by the action of *p*-bromonitrosobenzene on diphenylhydrazine; it crystallises in golden-yellow needles melting at 119—120°. J. J. S.

Nitro-derivatives of Azo-, Azoxy-, and Hydrazo-benzene. By ALFRED WERNER and EDMUND STIASNY (*Ber.*, 1899, 32, 3256—3282).—The details which follow show that nearly all the results obtained by Janovsky (*Abstr.*, 1886, 794) on nitrating azobenzene are incorrect. The so-called *p*-nitroazobenzene melting at 137° (compare Gerhardt and Laurent, *Annalen*, 1850, 75, 73; Klinger and Zuurdeeg, *Abstr.*, 1890, 761) consists in reality of a mixture of this compound with *p*-nitroazoxybenzene; in the nitration, a considerable quantity of *p*-dinitroazobenzene is also formed. Janovsky's "*o*-nitroazobenzene," melting at 127°, consists of a similar mixture.

The results obtained by Zinin (*Annalen*, 1841, 38, 222) on nitrating azoxybenzene are confirmed; the compound melting at 88·5°, obtained by reducing *o*-nitroazoxybenzene with alcoholic ammonium sulphide (Zinin, *loc. cit.*), is benzeneazonitrosobenzene, $C_6H_4 \begin{smallmatrix} N \\ \diagup \quad \diagdown \\ NO \end{smallmatrix} NPh$, which on reduction with stannous chloride and hydrochloric acid yields benzene- ψ -azimidobenzene, $C_6H_4 \begin{smallmatrix} N \\ \diagup \quad \diagdown \\ N \end{smallmatrix} NPh$ (m. p. 109°).

4:4'-Dinitroazobenzene melts at 121—122°. 3:3'-Dinitroazobenzene, prepared by reducing 3:3'-dinitroazoxybenzene (m. p. 146·5°, Klinger and Zuurdeeg, *loc. cit.*; Lobry de Bruyn, *Abstr.*, 1894, i, 573) with alcoholic ammonium sulphide, crystallises from alcohol in reddish needles and melts at 153°; the red oil obtained by Janovsky in the nitration of azobenzene, which was supposed to be dimetanitroazobenzene, is merely a mixture. Janovsky's *o**p*-dinitroazobenzene is also merely the impure 4:4'-dinitro-compound, and the same is true of his *mp*-dinitroazobenzene (m. p. 205°), obtained by acting with nitric acid on *p*-nitroazobenzene-*p*-sulphonic acid; the "dinitroazobenzene" melting at 180° is in reality impure 4:4'-dinitroazoxybenzene (*infra*). 2:4-Dinitroazobenzene can be prepared from the synthetically obtained 2:4-dinitrohydrazobenzene as stated by Willgerodt and Ferko (*Abstr.*, 1888, 829).

4:4'-Dinitroazoxybenzene, prepared by leaving 4:4'-dinitroazobenzene in contact with fuming nitric acid for half an hour, crystallises from benzene in stout, sulphur-yellow needles and melts at 192°.

All five of Janovsky's so-called trinitroazobenzenes are shown to be mixtures. That melting at 112° is a mixture of trinitroazoxybenzenes; that melting at 170°, obtained by nitrating *p*-nitroazobenzene, consists of a mixture of *o*- and *m*-trinitroazoxybenzene (Klinger and Zuurdeeg), whilst if the nitration is more carefully regulated, 4:4'-dinitroazoxybenzene (m. p. 185°) is principally formed. The trinitroazobenzene (m. p. 124°), obtained from the so-called *m*-dinitroazobenzene, is a mixture of trinitroazoxybenzenes; on nitrating 4:4'-dinitroazobenzene, either 4:4'-dinitroazoxybenzene (m. p. 185°) is obtained, or 2:4:4'-trinitroazoxybenzene (m. p. 135—136°, Klinger and Zuurdeeg), although

Janovsky has stated that under these conditions a trinitroazobenzene melting at 160° is formed. The "trinitroazobenzene" melting at 185° , obtained by nitrating 4:4'-dinitroazobenzene at a high temperature, is really 4:4'-dinitroazoxybenzene.

On energetically nitrating azobenzene, there is formed in addition to 2:4:2'-trinitroazoxybenzene (m. p. 192° ; Klinger and Zuurdeeg, 187— 188°), and 2:4:3'-trinitroazoxybenzene (m. p. 178°), a large proportion of 2:4:4'-trinitroazoxybenzene (m. p. 135 — 136°).

On reduction with ammonium sulphide, 4:4'-dinitroazobenzene gives rise to 4:4'-dinitrohydrazobenzene (m. p. 234°), not to Janovsky's so-called "azonitrolic" derivative (compare Lermontoff, Abstr., 1872, 503); as this substance dissolves in alkalis yielding blue salts, Willgerodt has assumed (Abstr., 1890, 1116) it to be an "azhydroxyazo-compound," $\text{NO}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{N} \cdot \text{N} \cdot \text{C}_6\text{H}_4 \cdot \text{NH}(\text{OH}) \cdot \text{O}$. Since, however, undoubted hydrazo-compounds which are soluble in alkali can be obtained by the interaction of phenylhydrazines with dinitrochlorobenzenes, Willgerodt's views must be rejected. The solubility or non-solubility in alkali of nitrohydrazo-compounds appears, indeed, to depend on the relative position of the nitro-groups; thus 2:4:4'-trinitrohydrazobenzene (*infra*) forms intensely blue salts with alkalis, whilst the 2:4:2'-trinitro-compound is insoluble in alkalis, although a blue coloration is produced on adding these to an acetone solution of the compound; 2:4:3'-trinitrohydrazobenzene fails to produce a coloration even in presence of acetone. Moreover, Willgerodt's views as to the conversion of nitrohydrazo-compounds into aznitroso-compounds by loss of water are incorrect; this decomposition is only possible with compounds which contain an ortho-nitro-group, and even with these in only a few cases. Thus although 2:4-dinitrohydrazobenzene in alcoholic solution is, by adding a drop of alkali, converted instantaneously into the compound
$$\text{NO}_2 \cdot \text{C} \begin{array}{c} \text{CH} \cdot \text{CH} \cdot \text{C} \cdot \text{N} \\ | \quad | \quad | \\ \text{CH} \quad \text{CH} \quad \text{C} \cdot \text{NO} \end{array} \text{NPh}, \text{ with } 2:4:2',$$
 2:4:3', and 2:4:4'-trinitrohydrazobenzenes no such conversion is possible.

4:4'-Dinitrohydrazobenzene melts and decomposes at 234° (compare Janovsky, Willgerodt, *loc. cit.*), and is readily oxidised to the corresponding azo-compound. 2:4-Dinitrohydrazobenzene (Willgerodt, *loc. cit.*) is converted by fuming nitric acid into 2:4:4'-trinitroazoxybenzene (m. p. 136°). 2:4:4'-Trinitrohydrazobenzene, prepared by the interaction of *p*-nitrophenylhydrazine with 1-chloro-2:4-dinitrobenzene, crystallises best from nitrobenzene in reddish-yellow, lustrous needles, and melts at 212 — 213° ; it is readily converted by mercuric oxide in alcoholic or acetone solution into 2:4:4'-trinitroazobenzene, which crystallises from glacial acetic acid in red needles, melts at 172° , and by oxidation with chromic acid is converted into Klinger and Zuurdeeg's trinitroazobenzene melting at 135 — 136° , the constitution of which is thus established. 2:4:3'-Trinitrohydrazobenzene, prepared from *m*-nitrophenylhydrazine and 1-chloro-2:4-dinitrobenzene, on oxidation with mercuric oxide, yields 2:4:3'-trinitroazobenzene (m. p. 172°), and with fuming nitric acid gives rise to 2:4:3'-trinitroazoxybenzene (m. p. 178° , Klinger and Zuurdeeg). 2:4:2'-Trinitrohydrazobenzene, prepared from *o*-nitrophenylhydrazine and 1-chloro-2:4-di-

nitrobenzene, crystallises from glacial acetic acid in bright yellow needles, melts at 220° , and is identical with the compound obtained by Klinger and Zuurdeeg on reducing trinitroazoxybenzene (m. p. 192°), which the latter considered to be the corresponding azo-compound; 2:4:2'-trinitroazobenzene, prepared by its oxidation, and also by reducing the corresponding azoxy-compound with ammonium sulphide, crystallises from alcohol in reddish needles and melts at 173° . Contrary to Klinger and Zuurdeeg's statement, the hydrazo-compound melting at 220° is readily acted on by fuming nitric acid, and converted into a substance which forms orange-red needles, melts at 220° , and is probably 2:4:2':4'-tetranitroazobenzene, although, owing to its explosive nature, it could not be analysed. W. A. D.

Preparation of Carbazides. Action of Phenolic Carbonates. By PAUL CAZENEUVE and MOREAU (*Compt. rend.*, 1899, 129, 1254—1257).—A mixture of hydrazine phenoxide and carbazide is produced by mixing diphenyl carbonate with an aqueous solution of hydrazine. Diphenylcarbazide is obtained in a similar manner from phenylhydrazine and diphenyl carbonate or guaiacyl carbonate.

Diphenyldimethylcarbazide, $\text{CO}(\text{NH}\cdot\text{NMePh})_2$, prepared by heating phenylmethylhydrazine with diphenyl carbonate at 160 — 170° , forms colourless needles melting at 149 — 150° .

$\beta\beta$ -*Dinaphthylcarbazide* is produced in small quantities by treating diphenyl carbonate (1 mol.) with β -naphthylhydrazine (4 mols.) at 100° ; the urethane, $\text{OPh}\cdot\text{CO}\cdot\text{NH}\cdot\text{NH}\cdot\text{C}_{10}\text{H}_7$, obtained when a smaller proportion of the hydrazine (2 mols.) is employed, crystallises in pale yellow spangles. G. T. M.

Formation of Methæmoglobin. By RICHARD VON ZEYNEK (*Chem. Centr.*, 1899, ii, 483—484; from *Arch. Anat. Phys.*, 1899, 460—490).—Spectrophotometric examination of alkaline solutions of crystallised methæmoglobin shows that this compound is optically well characterised as an individual substance. By the action of potassium ferricyanide on hæmoglobin, oxygen is liberated. The oxyhæmoglobin decomposes into hæmoglobin and oxygen; the place of the oxygen is taken by other elements or groups which confer weak acid properties for the colour of the compound so formed, and the spectrum of its aqueous solution are changed by the action of a small quantity of alkali. Oxygen is also liberated in the formation of methæmoglobin from oxyhæmoglobin by the action of potassium permanganate, but not by the action of sodium nitrite.

E. W. W.

Amylase. By PAUL YVON (*Ann. de l'Inst. Pasteur*, 1899, 13, 523—528. Compare *Abstr.*, 1895, i, 692).—By certain modifications in Lintner's method for the preparation of amylase, a better yield is obtained. H. R. LE S.

Organic Chemistry.

Oxidation of Organic Compounds with Alkaline Potassium Permanganate. By EDUARD DONATH and HUGO DITZ (*J. pr. Chem.*, 1899, [ii], 60, 566—576).—The authors conclude, from Berthelot's thermo-chemical considerations (*Annalen, Supp.*, 6, 187), that oxidations with acid permanganate are less energetic than those with an alkaline solution of the reagent. With concentrated permanganate, in acid solution and at high temperatures, the final products are usually carbon dioxide and water, but with alkaline permanganate the final product is oxalic acid, reactions which are in accord with Berthelot's third thermochemical law.

The authors question Berthelot's statement that formic acid is produced together with oxalic and carbonic acids in the oxidation of acetylene with alkaline permanganate, since this acid is so readily attacked by the alkaline permanganate that it has been recommended as a method for its estimation, and further, since sodium formate is often added to destroy excess of permanganate in oxidation processes.

Propylene, isobutylene, and amylene (Abstr., 1879, 246), ethyl alcohol (*Jahresber.*, 1867, 337), acetone (Abstr., 1899, i, 251), fatty acids (*Zeit. anal. Chem.*, 1886, 25, 588), butyric, lactic, succinic, and tartaric acids, lactose, dextrose, sucrose, all yield oxalic acid. Alkaline permanganate may be employed for estimating glycerol in fats, acetone in wood naphtha, and also for the estimation of lactic acid (Abstr., 1897, ii, 389). Benzene and toluene are not oxidised by alkaline permanganate; dimethylbenzenes, especially *o*-xylene, are readily oxidised, as also are sulphur compounds, such as carbon disulphide and thiophen—in fact, benzene may be readily freed from thiophen by the aid of alkaline permanganate.

J. J. S.

Products of the Explosion of Acetylene. By WILLIAM G. MIXTER (*Amer. J. Sci.*, 1900, 9, 1—9).—Acetylene is not completely decomposed into carbon and hydrogen by electric sparks, even when under a pressure of three atmospheres; the decomposition was, perhaps, somewhat more complete in the experiments made by Berthelot and Vieille, who used pressures varying from 5—30 atmospheres.

It is, however, probable that, after decomposition, a certain amount of acetylene is actually regenerated from the carbon and hydrogen. The residual acetylene was estimated by loss in volume after absorption in ammoniacal solution of cuprous chloride. In some experiments, where the gas was not free from nitrogen, traces of hydrocyanic acid were present; the absence of free cyanogen was somewhat doubtful.

L. DE K.

Action of Copper on Acetylene: Formation of Cuprene, a highly condensed Hydrocarbon. By PAUL SABATIER and JEAN B. SENDERENS (*Compt. rend.*, 1900, 130, 250—252. Compare Abstr., 1899, i, 555).—When acetylene is passed over copper heated at 180—250°, a mixture of hydrogen, unaltered acetylene, and volatile

hydrocarbons is produced; prolonged action causes the copper to swell and become converted into a yellow mass composed of microscopic filaments. This substance, when compressed, resembles tinder; it consists of a non-volatile hydrocarbon mixed with 1·7 to 3 per cent. of copper, the composition of the compound corresponding with the empirical formula C_7H_8 (compare Alexander, *Abstr.*, 1899, i, 843). The authors suggest the name *cuprene* for this hydrocarbon, on account of the mode of formation. The substance is insoluble in all the ordinary solvents, and is not attacked by sulphuric acid; with nitric acid, however, it yields nitro-derivatives; when heated above 400° , it decomposes into a mixture of volatile hydrocarbons, and leaves a residue of carbon; it burns with a smoky flame, at the same time evolving an aromatic odour.

G. T. M.

Action of Hydroxylamine on Dehydracetic Acid. By GAETANO MINUNNI (*Gazzetta*, 1899, 29, [ii], 452—466).—*Dehydracetic acid monoxime*, $C_8H_8O_3 \cdot N \cdot OH$, separates from alcohol in microscopic, rhombic laminae, and from benzene in needles; it is slightly soluble in acetone, acetic acid, or chloroform. It darkens at about 140° , and becomes almost black at 145° , melting and decomposing at 153 — 154° if heated rapidly, and at $149\cdot5$ — 150° or $150\cdot5$ — 151° with gentle heating. It dissolves readily in solutions of alkali hydroxides or carbonates and in concentrated sulphuric acid. When treated with acetic anhydride, it yields: (1) an *anhydride*, $C_8H_7O_3N$, which crystallises from dilute alcohol in long, white, slender needles melting at $150\cdot5$ — 151° ; (2) an isomeric *compound* separating from dilute alcohol in large, flattened needles having a pungent odour and melting at 124 — 125° .

Benzoyl chloride converts the monoxime into a *compound*, $C_8H_9O_4N$, which is isomeric with it, and crystallises from alcohol in flattened, white needles melting at $190\cdot5$ — 192° ; it gives the normal molecular weight in freezing acetic acid. In the presence of pyridine, the action of benzoyl chloride on the monoxime gives rise to the anhydride, $C_8H_7O_3N$, melting at $150\cdot5$ — 151° just described.

Dehydracetic acid dioxime anhydride, $C_8H_8O_3N_2$ ($= C_8H_8O_2(N \cdot OH)_2 - H_2O$), separates from aqueous alcohol in long, white, prismatic needles melting at 167 — 168° if gently heated, or at 172 — 173° on more rapid heating. After drying in the air and then over sulphuric acid, it has the composition $C_8H_8O_3N_2 + H_2O$; the mol. of water is lost over sulphuric acid in a vacuum.

T. H. P.

Isopyromucic Acid. By L. J. SIMON (*Compt. rend.*, 1900, 130, 255—257).—Isopyromucic acid was first isolated by Limpricht in 1873, who found that it accompanied its isomeride, pyromucic acid, in the product of the dry distillation of mucic acid; its existence was, however, denied by Oliveri and Peratoner (*Abstr.*, 1890, 1242).

The author finds that isopyromucic acid is produced by distilling a mixture of mucic acid and potassium hydrogen sulphate, and fractionating the aqueous distillate under diminished pressure; the acid passes over at about 100° under 20 mm. pressure, the yield being 20 per cent. of the theoretical. The acid is colourless when pure, and possesses an empyreumatic odour; it is readily soluble in alcohol, ether

chloroform, and hot benzene, but dissolves only sparingly in carbon disulphide. When crystallised from water, it contains $2\text{H}_2\text{O}$ and melts at $80\text{--}85^\circ$; the anhydrous acid is prepared by distillation or by crystallisation from benzene or chloroform, and melts at $90\text{--}95^\circ$. Cryoscopic and acidimetric determinations indicate that it has the molecular formula $\text{C}_5\text{H}_8\text{O}_3$. Neutral solutions of the acid, or its sodium and lead salts, develop an intense green coloration with ferric chloride, which is distinguishable even when the dilution corresponds with 1/10,000; the colour is destroyed by acids. The melting point, solubility, and ferric chloride reaction all agree with the properties of the acid as recorded by Limpricht.

G. T. M.

Acidimetry of Organic Polybasic Acids. By A. ASTRUC (*Compt. rend.*, 1900, 130, 253—254. Compare this vol., i, 141, 226; ii, 122).—The acidity of all di- and tri-basic organic acids towards phenolphthalein, Poirrier's blue, litmus, and rosolic acid corresponds with the number of carboxyl groups in the molecule. This is equally true whether the compounds are simple normal, or iso-acids, or whether they possess other functions due to the presence of hydroxyl, halogen, or unsaturated radicles.

The influence of these radicles and of the molecular weight on the acidity becomes apparent when methyl-orange is employed as the indicator. The acidity of oxalic, malonic, and succinic acids diminishes as the molecular weight increases; malonic and isosuccinic acid behave as monobasic acids, whilst succinic acid is neutralised by less than a molecular proportion of alkali, and sebacic acid is neutral. The results agree with Massol's thermochemical investigations on the heat of formation of the salts of these acids. The acidity of the phthalic acids, as indicated by methyl-orange, is greatest for the ortho- and least for the para-isomeride.

Maleic, fumaric, and acetylenedicarboxylic acids exhibit greater acidity than succinic acid, their saturated isologue; the two former are neutralised by one mol. of potassium hydroxide, whilst the acetylene derivative requires a greater amount of the alkali. Itaconic, mesaconic, and citraconic acids are monobasic towards methyl-orange and are therefore more acidic than the saturated dicarboxylic acids containing the same number of carbon atoms. Malic acid is monobasic under the same conditions, and tartronic acid requires for neutralisation even a greater proportion of the alkali; tartaric acid also is more acidic than succinic and malonic acids.

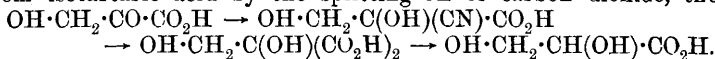
The heat of formation of the salts of these hydroxy-compounds is greater, and the heat of neutralisation of the free acid less, than the corresponding constants of the unsubstituted acids containing the same number of carbon atoms; the acidity, as indicated by methyl-orange, appears therefore to depend on the heat of formation of the salt, and not on the heat of neutralisation of the acid.

Tricarballic and citric acids furnish results in accordance with this generalisation. The presence of a halogen radicle in the molecule increases the acidity of the organic compound; trichloroacetic acid is distinctly monobasic towards methyl-orange, whilst dibromosuccinic acid is dibasic both with this indicator and with phenolphthalein.

G. T. M.

Optical Activity of Hydroxypyruvic Acid. By J. H. ABERSON (*Zeit. physikal. Chem.*, 1899, 31, 17—21).—Will's researches (*Abstr.*, 1891, 542) have not decided whether the constitution of this acid is to be represented by $\text{CHO}\cdot\text{CH}(\text{OH})\cdot\text{CO}_2\text{H}$ or $\text{OH}\cdot\text{CH}_2\cdot\text{CO}\cdot\text{CO}_2\text{H}$. The former constitution is supported by the fact that a solution of the acid, as obtained by Eder's method, is optically active; it reduces an alkaline silver solution easily, and Fehling's solution on warming; phenylhydrazine gives an osazone melting at $206-208^\circ$. Evaporation of this acid solution to dryness (in the course of which traces of oxides of nitrogen may be detected) and subsequent heating in the steam-bath reduces the specific rotation; on repetition of the process, the solution of the acid is no longer optically active, although it behaves in the same way with the reagents named, and an analysis of the calcium salt establishes the composition of the acid; the optical activity observed in the first instance therefore is doubtless due to some impurity containing nitrogen.

By heating the acid in a sealed tube with hydrocyanic acid, and subsequent treatment with hydrochloric acid and baryta, an easily soluble barium salt is obtained, which analysis shows to be barium glycerate; the properties of the free acid are those of glyceric acid, which is formed from isotartaric acid by the splitting off of carbon dioxide, thus:



It follows that hydroxypyruvic acid is a ketonic acid, for if it were an aldehydic acid, ordinary tartaric acid would have been formed, which does not lose carbon dioxide on heating. J. C. P.

Solubility in Water of Anhydrides of Organic Acids. By E. VAN DE STADT (*Zeits. physikal. Chem.*, 1899, 31, 250—254).—The author takes objection to the generally accepted notion that the anhydrides of organic acids are not dissolved by water until converted into the corresponding acids. From the results of time determinations of the solubility of phthalic acid and anhydride, and of succinic acid and anhydride, as well as of mixtures of the corresponding acid and anhydride, it is concluded that the anhydrides are soluble.

T. H. P.

Acidimetric Value of Substituted Malonic Acids compared with that of Corresponding Normal Dibasic Acids. By GUSTAVE MASSOL (*Compt. rend.*, 1900, 130, 338—340. Compare *Abstr.*, 1898, ii, 558; 1899, ii, 80, 143, 204, 353, 547).—A review of the author's previous work from which the following general conclusions are drawn:

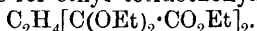
(1) For normal acids of the oxalic acid series, an increase of CH_2 produces a decrease in the acidimetric value corresponding with $2 - 1$ Cal. Starting from a C_5 acid, the heat of neutralisation goes on decreasing in value until a minimum is reached, and this takes place when the carboxyl groups are sufficiently distant to exert no influence on each other.

(2) Monosubstituted malonic acids behave like the acids of the oxalic series.

(3) The heat of neutralisation of a normal acid is less than that of a monosubstituted acid containing the same number of carbon atoms and consequently possessing the same molecular weight.

(4) The acidimetric value of dibasic acids depends much more on their structure and on the distance between the carboxyl groups than on their molecular weight.
H. R. LE S.

Electrolysis of Ethyl Potassium Diethoxysuccinate. By ALEXANDER CRUM BROWN and HERBERT W. BOLAM (*Proc. Roy. Soc. Edin.*, 1898, 22, 255—257).—Hitherto the method of electrolytic synthesis of dibasic acids has not been found to work where the anion contains a hydroxy- or ethoxy-group; in the case of ethyl potassium diethoxysuccinate, however, the method is applicable. Ethyl diethoxysuccinate was prepared by Purdie's method (*Trans.*, 1885, 47, 856; 1891, 59, 468) and also by the action of sodium ethoxide in alcoholic solution in the cold on ethyl dibromosuccinate; the product thus obtained is the unsymmetrical compound. The ethyl potassium salt, obtained from the ester by the action of alcoholic potash in the cold, was electrolysed (12 volts, 3—4 ampères), and an oil was formed, slightly soluble in water. Analysis of this oil gave numbers agreeing fairly closely with those for ethyl tetraethoxyadipate,



J. C. P.

Constitution of Saturated Dicarboxylic Acids. By GUSTAV KOMPPA (*Chem. Centr.*, 1899, ii, 1016—1017; from *Festsch. Polytech. Inst. Finnland*).—Undecane- $\alpha\lambda$ -dicarboxylic acid has been prepared from methyl undecenoate, $\text{CH}_2\text{:CH} \cdot [\text{CH}_2]_8 \cdot \text{CO}_2\text{Me}$, by treating the hydrogen bromide additive compound, $\text{CH}_2\text{Br} \cdot [\text{CH}_2]_9 \cdot \text{CO}_2\text{Me}$, with ethyl sodiomalonate, and finally removing carbon dioxide from the tricarboxylic acid so formed. This undecanedicarboxylic acid is not identical with brassylic acid obtained from brassidic, erucic, or behenoleic acid, hence all these acids probably contain a side chain. Since Nördlinger's decanedicarboxylic acid, prepared by the action of potassium cyanide on bromoundecoic acid, is the normal acid, $\text{CO}_2\text{H} \cdot [\text{CH}_2]_{10} \cdot \text{CO}_2\text{H}$, for it is identical with the acid obtained by the electrolysis of *n*-pimelic acid, it follows that the bromo-compound formed by the combination of hydrogen bromide with methyl undecenoate cannot have the composition $\text{CO}_2\text{Me} \cdot [\text{CH}_2]_8 \cdot \text{CHMeBr}$. Brassylic acid, prepared by the action of nitric acid on erucic acid, may be purified with great loss by distilling and crystallising the methyl ester; it melts at 114° . The methyl ester melts at 35° and boils at $326\text{—}328^\circ$. The amide melts at 177° . Undecane- $\alpha\lambda$ -dicarboxylic acid melts at 82° . The methyl ester is a liquid, and boils at $319\text{—}321^\circ$. The amide melts at $150\text{—}5^\circ$.

Methylundecenoate boils at 124° under 10 mm. pressure. Methyl bromoundecenoate boils at 165° under 10 mm., and at 158° under 6.5 mm. pressure. Methyl undecane- $\alpha\lambda\lambda$ -tricarboxylate, $\text{CO}_2\text{Me} \cdot [\text{CH}_2]_{10} \cdot \text{CH}(\text{CO}_2\text{Me})_2$, is an oil, boils at $223\text{—}224^\circ$ under 10 mm. pressure, and, when hydrolysed, yields an oily acid which is decomposed at 125° , liberating carbon dioxide and forming undecane- $\alpha\lambda$ -dicarboxylic acid, $\text{C}_{13}\text{H}_{24}\text{O}_4$. The latter acid separates from benzene as a crystalline powder, crystallises from alcohol in small, colourless needles, and dissolves in 9660 parts of water at 15° , but is much more soluble in organic solvents. The salt, $\text{C}_{13}\text{H}_{22}\text{O}_4\text{Ag}_2$, $\text{C}_{13}\text{H}_{22}\text{O}_4\text{Ba}$, forms a white, crystalline powder insoluble in water. The amide, $\text{C}_{13}\text{H}_{26}\text{O}_2\text{N}_2$, crystallises from dilute

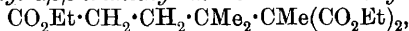
alcohol in short, colourless needles, and is insoluble in water, but easily soluble in hot alcohol. The *dimethyl* ester, $C_{15}H_{28}O_4$, is a rather viscous, colourless liquid, and has a sp. gr. 0.9697 at $20^\circ/20^\circ$.

The electrosynthesis of decanedicarboxylic acid was carried out by Crum Brown and Walker's method. The potassium ethyl salt of *n*-pimelic acid, obtained by partially hydrolysing the diethyl ester with alcoholic potassium hydroxide solution, on electrolysis yields gases which have a melon-like odour, together with an oily mass of diethyl decane- $\alpha\kappa$ -dicarboxylate. Decane- $\alpha\kappa$ -dicarboxylic acid, $C_{12}H_{22}O_4$, crystallises from hot water in slender needles and melts at $125.5-127^\circ$; 0.0059 part dissolves in 100 parts of water at 23° , and 0.105 in 100 of boiling water. The properties of this acid are identical with those of Nördlinger's acid. E. W. W.

Synthesis of Campholic Acid by means of Camphoric Acid. By ALBIN HALLER and G. BLANC (*Compt. rend.*, 1900, 130, 376—378. Compare Abstr., 1896, i, 385 and 448.)—When the campholide obtained by reducing camphoric anhydride with sodium amalgam is dissolved in anhydrous acetic acid and the solution saturated with hydrogen bromide, bromocampholic acid is precipitated in the form of white scales melting at 177° and is identical with the acid prepared by Baeyer and Villiger (this vol., i, 133) from the campholide obtained directly from camphor. Bromocampholic acid is converted by heating with zinc dust and acetic acid at $50-60^\circ$ into an acid identical in every respect with campholic acid. The converse transformation of campholic acid into camphor may be effected through camphoric acid, campholide, cyanocampholic acid, and homocamphoric acid. N. L.

Camphoric Acid. By LUIGI BALBIANO (*Gazzetta*, 1899, 29, ii, 490—592).—The author brings together and discusses his researches on camphoric acid (compare Abstr., 1893, i, 174; 1894, i, 614; 1895, i, 552; 1897, i, 253; 1899, i, 867). His results are all explainable by Bredt's formula for camphoric acid. T. H. P.

Camphoric Acid. Synthesis of a Camphor Derivative, 2:3:3-Trimethylcyclopentanone. By WILLIAM A. NOYES (*Ber.*, 1900, 33, 54—58. Compare Abstr., 1899, i, 284, 759).—A 6 per cent. yield of *ethyl* $\alpha\beta$ -trimethylbutane- $\alpha\alpha$ -dicarboxylate,



is obtained when the sodium derivative of ethyl methylmalonate is heated with an absolute alcoholic solution of ethyl γ -bromoisohexanoate. It distils at $170-180^\circ$ under 13—15 mm. pressure, and when hydrolysed with alcoholic potash yields the *acid*; this crystallises from ether in needles, melts at $185-190^\circ$, and at $190-200^\circ$ is converted into $\alpha\beta$ -trimethyladipic acid. When the latter acid is distilled with lime, it yields the 2:3:3-trimethylcyclopentanone previously obtained from *cis*-campholytic (isolauronic) acid, the constitution of which

must therefore be $\begin{array}{c} CMe_2 \cdot CMe \\ | \quad \quad | \\ CH_2 - CH_2 \end{array} > C \cdot CO_2H$ (compare Abstr., 1899, i, 928.) The author considers that this supports Perkin's first con-

stitution for camphoric acid (Proc., 1896, 12, 191) and Bouveault's formula for camphor (*Chem. Zeit.*, 1897, 21, 761). J. J. S.

Action of Ethyl Iodide on Diethyl Tartrate and Sodium Ethoxide. By JOHN E. BUCHER (*Amer. Chem. J.*, 1900, 23, 70—82. Compare Michael and Bucher, Abstr., 1896, i, 85, 599, and Lassar-Cohn, Abstr., 1887, 918).—The author has carefully examined the products obtained by acting on ethyl tartrate with ethyl iodide and sodium ethoxide under varying conditions, and has succeeded in proving that, besides the diethyl *as*-diethoxysuccinate shown to be present by Michael and Bucher (*loc. cit.*), some quantity of the *s*-diethoxy-derivative is also produced.

When diethyl tartrate (1 mol.) is boiled with sodium (2 ats.) dissolved in absolute alcohol, a yellowish-brown sodium compound separates, which, on decomposition with acid, yields an oil showing the characteristic reactions of a ketonic ester. On boiling the sodium compound with sodium hydroxide, a considerable quantity of sodium oxalate is obtained. The ketonic ester reacts with phenylhydrazine, and the product, on hydrolysis with alkali, gives a nearly colourless substance having the melting point of 1-phenyl-5-pyrazolone-3-carboxylic acid, and with ferric chloride the violet colour characteristic of that substance, but as the crystals of the compound differed in appearance from those prepared by other methods, the identity of the substance cannot as yet be regarded as established. A. L.

Malates and Tartromalates. By CHARLES ORDONNEAU (*Bull. Soc. Chim.*, 1900, [iii], 23, 9—15).—*Calcium α-tartromalate*, $C_4H_4O_6Ca + C_4H_2O_5Ca$, obtained by extracting crude calcium tartrate with boiling water, or by adding calcium acetate and excess of ammonia to a mixture of equal weights of malic and tartaric acids, crystallises in microscopic, silky needles containing 9—10H₂O at the ordinary temperature, and 6H₂O when dried at 100°. 100 c.c. of water at 20° dissolve 0.27 gram of the salt, which is decomposed by boiling water and by dilute acetic and hydrochloric acids.

Calcium α-malate is prepared by boiling crude calcium tartrate with a solution of tartaric acid, adding excess of lime, filtering from the precipitated calcium tartrate, tannin, &c., and evaporating the filtrate. The crystals contain 2H₂O at 100°; 100 c.c. of water dissolve 0.96 gram at 20° and 0.68 gram at 100°.

α-Tartromalic acid is obtained in crystals of the composition $C_4H_6O_6 + C_4H_6O_5$ by dissolving tartaric acid in excess of a hot, saturated solution of malic acid, or by boiling calcium α-malate with tartaric acid, filtering, and evaporating. When mixed with calcium acetate solution, it yields a precipitate of calcium tartrate, but if the acid is previously neutralised with ammonia, calcium α-tartromalate is formed.

Calcium hydrogen malate, $(C_4H_5O_5)_2Ca + 3H_2O$, is obtained by treating crude calcium tartrate or calcium malate with the calculated amount of dilute sulphuric acid; the crystals lose 2H₂O at 100°. 100 grams of water dissolve 2.93 grams of the salt at 20°; the concentrated solution is partially decomposed by boiling, and calcium

β -malate is precipitated, but when lime is added to a boiling solution calcium α -malate is formed.

Calcium β -malate is best prepared by boiling calcium hydrogen malate with an equal weight of water; at 80° , a clear solution is obtained, but above that temperature precipitation occurs. Calcium β -malate crystallises with $2\text{H}_2\text{O}$ and is converted by dilute sulphuric acid into ordinary calcium hydrogen malate; when dissolved in hydrochloric acid and saturated with ammonia, crystals of calcium α -malate slowly separate.

Calcium β -tartromalate, prepared by adding calcium acetate to a solution in dilute hydrochloric acid of equal weights of calcium tartrate and β -malate, has the same formula as the corresponding α -salt, but crystallises in rhombic plates; the crystals contain $6\text{H}_2\text{O}$ at 100° .

β -Tartromalic acid, a stable, crystalline compound, is extracted from certain manufactory residues. The calcium hydrogen malate obtained from this acid, after elimination of the tartaric acid by means of potash, reacts with tartaric acid to form calcium α -tartromalate. N. L.

Oxidation of Citric and Malic Acids by Potassium Permanganate. By GEORGES DENIGÈS (*Compt. rend.*, 1900, 130, 32—35).—Citric acid in aqueous solution is oxidised by potassium permanganate at the ordinary temperature with production of carbon dioxide and acetonedicarboxylic acid, which can be isolated by precipitation with mercuric sulphate. A small quantity of oxalic acid is also formed.

If the permanganate is carefully added to a hot solution of malic acid, excess being avoided, there is no liberation of carbon dioxide and oxalacetic acid is formed; this can be precipitated by mercuric acetate solution, which has no effect on malic acid.

In both cases, the permanganate attacks the alcoholic group of the acid, with production of a complex ketone. C. H. B.

Phenylhydrazine Derivatives of Glycuronic Acid. By PAUL MAYER (*Zeit. physiol. Chem.*, 1900, 29, 59—69. Compare Thierfelder, 1887, 235, 717; 1889, 378; Hirschl, 1890, 835).—Glycuronic acid, obtained from Indian yellow by Mann and Tollens' method (*Abstr.*, 1896, i, 417), has been treated with 1, 2, 3, and 4 mols. of phenylhydrazine in acetic acid solution. In all cases, a certain amount of tarry matter is produced, but with 1 mol. a compound crystallising in small needles and melting at 210 — 217° is formed. Its composition agrees with that of glucosazone. When an excess of phenylhydrazine is employed, a compound melting at 159 — 164° is obtained; although the melting point of this compound is identical with that of pentosazone, it is not a pentosazone, as it contains 11.5, instead of 17.07, per cent. of nitrogen.

From these facts, it follows that phenylhydrazine is of no use as a reagent for glycuronic acid. Bromophenylhydrazine, on the other hand, yields an extremely characteristic compound with glycuronic acid (*Abstr.*, 1899, i, 933), and is probably the best reagent to employ for the detection of the acid. J. J. S.

Formaldehyde- or Methylene-derivatives of Acids belonging to the Sugar Group. By G. H. A. CLOWES and BERNHARD TOLLENS (*Annalen*, 1899, 310, 164—189. Compare Weber and Tollens, *Abstr.*, 1898, i, 60).—In preparing monobasic acids of the sugar group by oxidising a glucose with bromine, it is better to add the calcium carbonate before the halogen, instead of afterwards; the lactone hydrate of galactonic acid, prepared by this method, melts at 66°, and has $[\alpha]_D - 67.9^\circ$ (compare Schnelle and Tollens, *Abstr.*, 1892, 1432).

Dimethylenegalactonic acid, $C_6H_8(CH_2)_2O_7$, prepared from galactonic acid and formaldehyde under the influence of hydrochloric acid, separates from acetone in crystals melting at 136°, and containing $2H_2O$ or $1H_2O$, according as the substance is dried in air or at 40°; it dissolves in 112 parts of water, and a 0.64 per cent. solution has the specific rotatory power $[\alpha]_D + 45.3^\circ$. The *potassium* and *sodium* salts contain $1H_2O$, and the *zinc*, *strontium*, and *copper* salts crystallise with $2H_2O$; the *phenylhydrazine* salt crystallises in needles, and melts at 208°.

Methylene-d-mannonic lactone, $C_6H_8O_6 \cdot CH_2$, obtained from mannonic acid and formaldehyde, crystallises from acetone and melts at 206°; a 1 per cent. solution has $[\alpha]_D + 91^\circ$. *Methylene-l-mannonic lactone*, $C_6H_8O_6 \cdot CH_2$, melts at 205—207°, and has $[\alpha]_D - 88^\circ$.

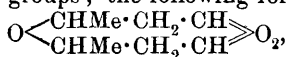
Xylonic lactone, $C_5H_8O_5$, produced on evaporating an aqueous solution of xylonic acid, crystallises from acetone and melts at 90—92°; a 0.8 per cent. solution has $[\alpha]_D + 74.4^\circ$. *Dimethylenexylonic acid*, $C_5H_8(CH_2)_2O_6$, obtained from calcium xylonate, formaldehyde, and hydrochloric acid, melts at 209—212°, and sublimes without appearing to change; it separates from water with $\frac{1}{2}H_2O$, and a 7.5 per cent. solution has $[\alpha]_D + 39.5^\circ$. The *zinc* and *calcium* salts contain $3\frac{1}{2}H_2O$ and $4H_2O$ respectively, and the *phenylhydrazine* salt is stable in air, but decomposes when gently heated.

Arabonic acid has no great tendency to form a methylene derivative, and it is doubtful whether it combines with formaldehyde.

The paper concludes with a complete list of methylene derivatives from acids of the sugar group, and a theoretical discussion by one of the authors (Tollens) relative to the manner in which the methylene group enters the molecule of a polyhydric alcohol or acid, and the position which it occupies. M. O. F.

Action of Potassium Cyanide on Aliphatic Aldehydes. II. By LEOPOLD KOHN (*Monatsh.*, 1899, 20, 903—908. Compare *Abstr.*, 1899, i, 328).—Potassium cyanide reacts vigorously with a solution of formaldehyde. If the temperature of the mixture is not allowed to rise above 30°, hexamethylenetetramine and potassium glycollate are formed. R. H. P.

Isodialdane. By CORNELIS G. LOBRY DE BRUYN and H. C. BIJL (*Proc. K. Akad. Wetensch. Amsterdam*, 2, 143—146).—Isodialdane, obtained by the condensation of aldol in the presence of hydrogen cyanide (Wurtz, *Bull. Soc. Chim.*, 1884, 42, 161), contains neither hydroxyl nor carbonyl groups; the following formula,



best expresses its constitution. This system is very stable, except under the action of dilute acids. There is some analogy between this compound and cane sugar, and the authors propose a formula for the latter, having a similar configuration. G. T. M.

Condensation of Glyoxal and Isobutaldehyde. By ERICH VON HORNPOSTEL and EDUARD O. SIEBNER (*Monatsh.*, 1899, 20, 835—836. Compare Abstr., 1896, i, 403).—When glyoxal (1 mol.) and isobutaldehyde (2 mols.), dissolved in alcohol, are condensed by the action of potassium carbonate in strong, aqueous solution and the mixture is distilled, two fractions with the composition $C_{10}H_{18}O_4$ are obtained. The first distils at 110° under 21 mm. pressure and has a vapour density corresponding with the molecular weight 202; the second is crystalline, melts at 54° , boils at 139° , and has a vapour density corresponding at first with the molecular weight 404, but after longer heating with 202. Under suitable conditions, both fractions appear to change, each into the other. Oxidation of this substance with potassium permanganate solution produces dimethylmalonic acid and a small quantity of a ketone, probably diisopropyl ketone. No reaction occurs with hydroxylamine or with phenylhydrazine. On reduction, a colourless, crystalline substance of the empirical composition, $C_{10}H_{19}O_4$, is obtained, which melts at 123 — 124° , and boils at 184° under 16 mm. pressure; this is also formed when glyoxal and isobutaldehyde are condensed with alcoholic potash.

The compound $C_{10}H_{18}O_4$ energetically reduces ammoniacal silver solution, whilst the reduction product, $C_{10}H_{19}O_4$, has only slight action on it. Both fail to absorb bromine. R. L. J.

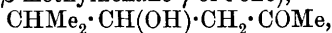
Action of Caro's Reagent on Ketones. By ADOLF BAEYER and VICTOR VILLIGER (*Ber.*, 1900, 33, 124—126).—If hydrogen peroxide is mixed with five times its volume of concentrated sulphuric acid, a reagent is obtained, which has an action on ketones such as acetone and tetrahydrocarvone, similar to that of Caro's reagent (see this vol., i, 133). When diluted with water, the reagent at once precipitates iodine from potassium iodide, whilst a mixture of hydrogen peroxide with dilute sulphuric acid does not do this; the authors therefore conclude that the liquid contains an acid analogous to 'chamber crystals,' to which they give the name of 'Caro's acid.'

By the action of Caro's reagent on diethyl ketone, an explosive oil is obtained, which has a pungent odour, immediately liberates iodine from potassium iodide, and is regarded as a simple *diethyl ketone peroxide*, CO_2Et_2 ; if allowed to remain longer in contact with the reagent, or if distilled under the ordinary pressure, it is converted into an oily *polymeride*, which has an ethereal smell and is indifferent to potassium iodide. Dipropyl ketone behaves similarly, and it is supposed that, in the case of acetone also, the first product is an active peroxide which subsequently polymerises. All the polymeric peroxides are decomposed by sulphuric acid, giving rise to the simple peroxides, the formation of which is indicated by their irritating odour and action on potassium iodide paper. T. M. L.

Isobutyridene-acetone and its Derivatives. By ADOLF FRANKE and LEOPOLD KOHN (*Monatsh.*, 1899, 20, 876—902. Compare Abstr., 1899, i, 10).—The condensation of isobutaldehyde and acetone belongs

to the class of "aldol" condensations, in which the oxygen atom of the aldehyde is eliminated as water. The resulting compound, *isobutylideneacetone*, $\text{CHMe}_2 \cdot \text{CH} : \text{CH} \cdot \text{COMe}$, is a colourless, repulsive smelling liquid, which boils at 157° (corr.) under 750 mm. pressure and at 51° under 16 mm. pressure. In common with most condensation products of aldehydes or aldehydes and ketones, it gives low results on combustion. It yields an unstable *dibromo*-derivative, $\text{C}_7\text{H}_{12}\text{OBr}_2$, and on treatment with bromine and dilute potash yields $\alpha\beta$ -isohexenoic acid (Abstr., 1896, i, 595). On oxidation with cold 1 per cent. solution of potassium permanganate, it yields isopropylglyoxylic acid. The *oxime* boils at 103° under 15 mm. pressure, and on treatment with acetic anhydride yields an *acetyl* derivative, which is a colourless liquid boiling at 132° under 16 mm. pressure, and on further treatment with acetic anhydride yields a crystalline compound melting at 84° .

Isobutyralacetone (β -methylhexane- γ -ol- ϵ one),



obtained as an intermediate product in the above condensation, or when isobutaldehyde and acetone are allowed to remain over a concentrated solution of potassium carbonate, is an oily, viscous liquid, which boils at 90° under 16 mm. pressure, and is easily converted into isobutylideneacetone; it yields an *oxime*, which is a thick, yellowish oil boiling at 126 — 129° under 16 mm. pressure. R. H. P.

Arabinose, Xylose, and Fucose from Tragacanth. By JOHN A. WIDSTOE and BERNHARD TOLLENS (*Ber.*, 1900, 33, 132—143).—Three samples of white tragacanth, when hydrolysed, yielded fucose and arabinose, whilst fucose and xylose were obtained from two samples of brown tragacanth. Determinations of the specific rotation of fucose derived from tragacanth and from *Fucus* (Tollens, Günther, and Chalmot, Abstr., 1892, 1352) gave values of $[\alpha]_D$ varying from -72° to -74.5° . R. H. P.

Complete Synthesis of the Phorone derived from Camphoric Acid. By LOUIS BOUVEAULT (*Compt. rend.*, 1900, 130, 415—417).—The action of α -methylcyclopentanone (this vol., i, 171) on acetone in the presence of sodium ethoxide results in the formation of

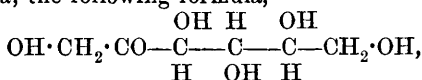
phorone, $\text{CMe}_2 : \text{C} \begin{array}{l} \text{CO} - \text{CHMe} \\ | \\ \text{CH}_2 \cdot \text{CH}_2 \end{array}$, which was identified with the pro-

duct described by Koenigs and Eppens (Abstr., 1892, 626; 1893, i, 361), both by its physical properties and by the preparation of its oxime and tribromo-derivative. The former crystallises in slender needles, sublimes very quickly on heating, and melts at 117° in a capillary tube and at 125° on mercury (Koenigs and Eppens give 121°); it has the composition $\text{C}_9\text{H}_{14} \cdot \text{N} \cdot \text{OH} + \text{H}_2\text{O}$, as pointed out by Kerp (Abstr., 1896, i, 446), and the presence of the mol. of water indicates that the ethylenic linking in phorone is in the α -position with respect to the carbonyl group. The tribromo-derivative melts at 48° (Koenigs and Eppens give 49 — 52°) and has the composition $\text{C}_9\text{H}_{13}\text{OBr}_3$, and not $\text{C}_9\text{H}_{11}\text{OBr}_3$. N. L.

The Resolution of Racemic Compounds into Active Components. By WILHELM MARCKWALD and ALEX. MCKENZIE (*Ber.*, 1900, 33, 208—210. Compare Abstr., 1899, ii, 733).—In reply to the

criticism of E. Fischer (this vol., i, 140), the authors maintain their claim to the novelty of the method employed by them for the resolution of racemic compounds. A. H.

d-Sorbinose and *l*-Sorbinose (ψ -Tagatose) and their Configurations. By C. A. LOBRY DE BRUYN and WILLIAM ALBERDA VAN EKENSTEIN (*Proc. K. Akad. Wetensch. Amsterdam*, 1899, 2, 268—271).—The ketose ψ -tagatose, obtained by the action of alkalis on galactose, is shown to be *l*-sorbinose. It is purified from *d*-tagatose by conversion into its anilide; when pure, it has α_D 42.3°, whilst that of its antipode is -42.7°; their solutions exhibit a slight birotation. The two ketoses are crystallographically identical, and have the same melting point, specific gravity, and solubility in water and the alcohols; when mixed in equal proportion, they yield a well-crystallised racemic compound; their osazones have the same melting point, 150—151°, and *l*-sorbinosazone is identical with *l*-gulosazone. On reduction with sodium amalgam, *d*-sorbinose yields *d*-sorbitol and *d*-iditol, whilst the corresponding alcohols of the *l*-series are obtained from *l*-sorbinose. From these data, the following formula,



has been deduced for *l*-sorbinose.

G. T. M.

Inverting Power of Tartaric, Citric and Oxalic Acids on Sucrose. By H. GILLOT (*Exper. Stat. Record*, 1899, 11, 20; from *Bul. Assoc. Belge Chim.*, 1899, 13, 80—94 and 119—130).—Tartaric acid has a greater inverting power than citric acid, and oxalic acid a greater power than either. The amount of sugar inverted increases considerably with the temperature, amount of acid, and concentration of the solution. N. H. J. M.

Arabic Acid from Beetroot. By EMIL VOTOCEK and J. ŠEBOR (*Chem. Centr.*, 1899, ii, 1022—1023; from *Zeits. Zuck.-Ind. Böhm.*, 24, 1—15).—Arabic acid, prepared by boiling beetroot pulp with alkalis, is not a homogeneous compound, but is a mixture of neutral substances. The preparations from different materials have different rotatory powers, and also yield varying amounts of arabinose and galactose. Moreover, by hydrolysing the acetyl derivatives of the acid, the original acid is not regained, but the products formed have a greater levorotatory power and contain different proportions of the groups which yield arabinose and galactose. The salts of arabic acid are to be regarded as alcoholates. Whilst lactobionic acid and maltobionic acid, &c., on hydrolysis yield large quantities of a hexonic acid and hexose, arabic acid, under similar conditions, does not form acid products, but only dextrorotatory substances which are insoluble in alcohol; arabinose and α -glucose were detected. The three constituents of arabic acid, araban, galactan and glucosan, may not be separate components of the acid, but may possibly form mixed complexes.

The rotatory power of arabic acid is only very slightly increased by lead acetate. E. W. W.

Caramel Substances. By F. STOLLE (*Chem. Centr.*, 1899, ii, 1021—1022; from *Zeit. Ver. Rübenzuck.-Ind.*, 1899, 800—807).—Caramel, $C_{12}H_{18}O_9$, prepared by heating the best refined sugar at 180 — 190° , and removing the undecomposed sugar by fermentation with yeast, is a reddish-brown, amorphous mass, has a conchoidal fracture, is easily soluble in water and melts at 134 — 136° . It is formed from sugar by the elimination of $2H_2O$, and is thus identical with Gélis's caramelan. By treating a concentrated solution of caramelan with ammoniacal lead acetate as long as a precipitate is formed, a compound, $C_{12}H_{16}O_9Pb$, is obtained. *Tetracetylcaramelan*, $C_{12}H_{14}Ac_4O_9$, prepared by the action of sodium acetate and acetic anhydride, is a dirty brown powder, and is insoluble in water, alcohol, or ether. *Benzoylcaramelan*, $C_{12}H_{17}BzO_7$, obtained by the action of benzoyl chloride on a strongly alkaline solution of caramelan, separates as a brown, nodular precipitate which is insoluble in light petroleum, alcohol, or ether, but soluble in glacial acetic acid, concentrated hydrochloric acid, or benzene. E. W. W.

Action of Hydrogen Peroxide on Aliphatic Amines. By LEONARD MAMLOCK and RICHARD WOLFFENSTEIN (*Ber.*, 1900, 33, 159—161).—The same results as those obtained by the authors on oxidising dipropylamine and tripropylamine with aqueous hydrogen peroxide have already been published by Dunstan and Goulding (*Trans.*, 1899, 75, 1004). The following facts, however, are new.

Dipropylhydroxylamine, $NPr_2 \cdot OH$ boils at 72 — 74° under 30 mm. pressure, and solidifies in the receiver to a white, crystalline mass; on reduction with zinc and hydrochloric acid, it yields dipropylamine, and is converted by sulphurous acid into *dipropylsulphamic acid*, $NPr_2 \cdot SO_3H$, which separates from benzene and light petroleum in white crystals and melts at 135° .

On being heated, tripropylamine oxide (tripropylloxamine, Dunstan and Goulding, *loc. cit.*) gives rise to dipropylhydroxylamine and propylene, along with tripropylamine; on heating in a vacuum, the first two products only are formed. Since dipropylhydroxylamine is easily reduced to dipropylamine, a simple method is afforded of passing from a tertiary to a secondary amine. W. A. D.

Ethylenediamine Compounds of Nickel. By NICOLAI A. KURNAKOFF (*Zeit. anorg. Chem.*, 1900, 22, 466—470).—When ethylenediamine is added to an aqueous solution of nickel chloride, a blue solution is at first obtained which, on the addition of more ethylenediamine becomes violet. The violet solution contains triethylenediamine nickel chloride, already described by Werner (*Abstr.*, 1899, i, 856). The blue solution contains *diethylenediaminenickel chloride*, which cannot be obtained crystalline. The *platinosochloride*, however, crystallises in six-sided, orange-red prisms; the *platinichloride* in small, orange-yellow, quadratic plates. E. C. R.

Ethylenediamine Compounds of Palladium. By NICOLAI A. KURNAKOFF and N. J. GWOSDAREFF (*Zeit. anorg. Chem.*, 1899, 22, 384—386).—Potassium palladochloride, when treated with ethylenediamine, yields a rose-coloured precipitate (probably $PdCl_2 \cdot 2C_2N_2H_8 \cdot PdCl_2$) which dissolves in excess of ethylenediamine and is converted into the compound $PdCl_2 \cdot 2C_2N_2H_8$, which separates

in colourless, prismatic crystals. This compound, unlike the corresponding platinum compound, when treated with dilute hydrochloric acid loses ethylenediamine, and is converted into the compound $\text{PdCl}_2 \cdot \text{C}_2\text{N}_2\text{H}_8$, which crystallises in small, yellow needles, is sparingly soluble in water, and when treated with thiocarbamide yields the compound $\text{PdCl}_2 \cdot 4\text{CSN}_2\text{H}_4$. When dissolved in strong hydrochloric acid, it is converted into *ethylenediammonium palladochloride*,
 $\text{PdCl}_2 \cdot \text{C}_2\text{N}_2\text{H}_{10}\text{Cl}_2$.

The latter crystallises in large, reddish-brown plates, decomposes when dissolved in water with loss of hydrogen chloride, and can be recrystallised without decomposition from hydrochloric acid. E. C. R.

Ethyl Bromoaminocrotonate. By ROBERT BEHREND and HERMANN SCHREIBER (*Ber.*, 1900, 33, 265—266. Compare Chattaway and Orton, this vol., i, 152).—*Ethyl β-bromoaminocrotonate*, obtained either by mixing ethereal solutions of acetylbromoamide and ethyl β-aminocrotonate, or by treating the latter with sodium hypobromite, crystallises from light petroleum in thick prisms or in needles; both modifications melt at 72—74°, but in each case, when the determination is repeated, the melting point is found to be 50°; a mixture of the two forms also melts at the lower temperature. The compound liberates iodine from an acidified solution of potassium iodide; this shows that it contains bromine attached to nitrogen. When treated with dilute sulphuric acid, ammonia is eliminated from the molecule, and ethyl α-bromoacetoacetate results. Ethyl β-chloroaminocrotonate (m. p. 53°) is formed by the action of acetylchloroamide or sodium hypochlorite on ethyl β-aminocrotonate. G. T. M.

α-Dichlorothiopropionamide. By JULIUS TROEGER and ERICH EWERS (*J. pr. Chem.*, 1899, [ii], 60, 520—523).—*α-Dichlorothiopropionamide*, $\text{CMeCl}_2 \cdot \text{CS} \cdot \text{NH}_2$ or $\text{CMeCl}_2 \cdot \text{C}(\text{SH}) \cdot \text{NH}_2$, obtained by the action of hydrogen sulphide on an alcoholic solution of α-dichloropropionitrile in presence of a small quantity of ammonia, crystallises in pale yellow plates, melts and decomposes at about 54°, is soluble in alcohol or ether, and is extremely unstable. E. G.

[Nitrosoalkylurethanes]. By JULIUS W. BRÜHL (*Ber.*, 1900, 33, 122—124).—A reply to Hantzsch in defence of the spectrometric method of determining the constitution of nitrogen compounds. T. M. L.

Thiocyanocobaltammonium Compounds. By JAN VON ZAWIDZKI (*Zeit. anorg. Chem.*, 1900, 22, 422—423).—A thiocyanocobaltamine chloride is obtained by adding ammonium thiocyanate to a solution of cobalt carbonate in hydrochloric acid, and after the addition of ammonia, oxidising the mixture with air. It crystallises in dark green to black needles, is very unstable, gives off ammonia in the air or in solution, being converted into a reddish powder, and when dissolved in acetic acid and treated with hydrochloric acid yields a blue precipitate. Cobalt nitrate and sulphate yield similar crystalline compounds (Werner, this vol., i, 86). E. C. R.

Condensation Products of Rubeanic Acid [Dithio-oxamide] with Aldehydes and Secondary Bases. By OTTO WALLACH (*Chem. Centr.*, 1899, ii, 1024—1026; from *Nachr. k. Ges. Wiss. Göttingen*, 1899, No. 2).—When rubeanic acid [dithio-oxamide] (1 mol.) is condensed with aldehydes, $\text{R} \cdot \text{CHO}$ (2 mols.), and secondary bases, NHR'_2 ,

compounds of the type $(\text{CNSH}\cdot\text{CHR}\cdot\text{NR}'_2)_2$ are formed; the products of the reaction yield lead salts, and therefore contain SH groups (Abstr., 1880, 556). Henry found that formaldehyde combines directly with secondary amines, hence the dithio-oxamide is assumed to act on these additive products, $\text{OH}\cdot\text{CH}_2\cdot\text{NR}_2$, in the pseudo-form $\text{SH}\cdot\text{C}(\text{NH})\cdot\text{C}(\text{NH})\cdot\text{SH}$, forming $\text{C}_2(\text{N}\cdot\text{CH}_2\cdot\text{NR})_2(\text{SH})_2$, with elimination of $2\text{H}_2\text{O}$. The products obtained by the combination of aldehydes and primary bases decompose with elimination of water, and the resulting compounds do not react with dithio-oxamide. These condensation products easily decompose into their components, and are only formed under certain conditions. The aldehyde and base are best dissolved in chloroform and the solution then shaken with dithio-oxamide. In some cases, the mixture requires heating on the water-bath.

The compounds $\text{C}_{14}\text{H}_{26}\text{N}_4\text{S}_2$, $\text{C}_{16}\text{H}_{30}\text{N}_4\text{S}_2$, $\text{C}_{22}\text{H}_{34}\text{N}_4\text{S}_2$, and $\text{C}_{26}\text{H}_{34}\text{N}_4\text{S}_2$ are prepared by condensing formaldehyde, acetaldehyde, valeraldehyde, and benzaldehyde respectively with piperidine and dithio-oxamide. The first compound crystallises in yellowish-red needles and melts at 143° ; the second forms needles, is very unstable, and melts at 90° ; the third separates in yellow crystals and melts at 119° , and the fourth forms pale yellow needles and melts at $110\cdot5^\circ$. By the action of formaldehyde and benzaldehyde on methylaniline and dithio-oxamide, the compounds $\text{C}_{18}\text{H}_{22}\text{N}_4\text{S}_2$ and $\text{C}_{30}\text{H}_{30}\text{N}_4\text{S}_2$ are formed respectively. The former crystallises in long, red needles and melts at 139° , whilst the latter forms pale yellow needles and melts at 154° . The compound $\text{C}_{20}\text{H}_{26}\text{N}_4\text{S}_2$, obtained from formaldehyde, ethylaniline, and dithio-oxamide crystallises in large, yellowish-red needles and melts at 107° . The compound $\text{C}_{32}\text{H}_{34}\text{N}_4\text{S}_2$, prepared from formaldehyde, dibenzylamine, and dithio-oxamide, forms large needles and melts at 123° .

The products of the condensation of formaldehyde and diethylamine, of valeraldehyde and diethylamine, of formaldehyde and dipropylamine, and of formaldehyde and diamylamine with dithio-oxamide are red oils. Benzaldehyde, diethylamine, and dithio-oxamide form a compound, $\text{C}_{24}\text{H}_{34}\text{N}_4\text{S}_2$, which crystallises in small, pale yellow needles and melts at 165° . The compound $\text{C}_{36}\text{H}_{58}\text{N}_4\text{S}_2$, prepared from benzaldehyde, diamylamine, and dithio-oxamide, forms yellow crystals and melts at 160° .

The lead compounds are obtained by mixing the alcoholic solution of the compound with an alcoholic solution of lead acetate.

By the condensation of substituted dithio-oxamides with aldehydes and secondary bases, compounds of the type $\text{C}_2\text{S}_2(\text{NR}\cdot\text{CHR}\cdot\text{NR}'_2)_2$ are formed, and these substances do not yield lead compounds. The compound $\text{C}_2\text{S}_2(\text{NMe}\cdot\text{CH}_2\cdot\text{NMePh})_2$, prepared from dimethyldithio-oxamide, formaldehyde, and methylaniline, crystallises in yellowish-red needles and melts at 141° . The compound $\text{C}_2\text{S}_2(\text{NMe}\cdot\text{CH}_2\cdot\text{NEtPh})_2$, similarly obtained from ethylaniline, separates in large, red plates and melts at 108° . The compound $\text{C}_2\text{S}_2(\text{NEt}\cdot\text{CH}_2\cdot\text{NEtPh})_2$, prepared from diethyldithio-oxamide, formaldehyde, and methylaniline, forms yellow needles and melts at 134° . Dithio-oxamides which contain aromatic groups, such as diphenyldithio-oxamide, do not form condensation products.

E. W. W.

Rhodicyanides. By ÉMILE LEIDIÉ (*Compt. rend.*, 1900, 130, 87—90).—Potassium rhodicyanide, $K_6Rh_2(CN)_{12}$, is best obtained by first preparing a saturated solution of recently precipitated hydrated rhodium sesquioxide in a 25—30 per cent. solution of potassium hydroxide, diluting with water until a precipitate of the sesquioxide appears, and then pouring the whole into an excess of a 20—25 per cent. solution of hydrocyanic acid. The mixture is allowed to remain for some time out of contact of air, filtered, the filtrate evaporated in a vacuum, and the salt which separates purified by recrystallisation. This compound belongs to the same class as the ferricyanides, cobaltcyanides, &c., for (1) not only is it isomorphous with these compounds, but it has the same optical properties, the same crystallographical angles, &c.; (2) it is decomposed by caustic potash, by concentrated hydrochloric acid with evolution of hydrocyanic acid, and by mercuric oxide with formation of potassium hydroxide, mercuric cyanide, and rhodium sesquioxide, and, lastly, with certain metallic salts it gives precipitates which are characteristic of this class of compounds.

H. R. LE S.

Transformation of Bisisopropylazimethylene [Isobutaldazine] into 4 : 4-Dimethyl-5-isopropylpyrazoline. By ADOLF FRANKE (*Monatsh.*, 1899, 20, 847—875. Compare Abstr., 1899, i, 329).—Isobutaldazine is easily prepared by the action of an aqueous solution of hydrazine sulphate (1 mol.) and sodium carbonate (1 mol.) on pure isobutaldehyde (2 mols.). It forms an argentonitrate, $C_8H_{16}N_2 \cdot AgNO_3$, which melts and decomposes at about 115° , and also yields an indefinite, white, crystalline substance on treatment with ethyl iodide. On warming with dilute hydrochloric or dilute sulphuric acid, or by the action of concentrated sulphuric acid in the cold, it is decomposed with re-formation of the aldehyde and a hydrazine salt; on treatment, however, with concentrated hydrochloric, fuming hydriodic, or maleic acid (compare Curtius and Zinckeisen, Abstr., 1899, i, 165), it is converted into a salt of 4 : 4-dimethyl-5-isopropylpyrazoline. 4 : 4-Dimethyl-5-isopropylpyrazoline, prepared by treating any of its salts with dilute alkalis, is a clear and somewhat viscous oil boiling at 202.5° (corr.), which has a camphor-like odour and is still liquid at -20° . The *hydrochloride*, prepared by the action of concentrated hydrochloric acid on isobutaldazine, forms transparent, colourless, monoclinic, holohedral crystals melting at 149° ; its aqueous solution colours woody tissue an intense yellow, but gives no coloration with potassium dichromate and sulphuric acid, thus showing that Knorr's reaction is only given by pyrazolines containing a phenyl group. The *hydriodide* obtained in the above manner forms colourless crystals. The *acetyl* derivative, $C_8H_{15}N_2Ac$, is a thick oil boiling at $120—125^\circ$ under 19 mm. pressure, and the *benzoyl* derivative crystallises in the form of small needles melting at 70° . The pyrazoline forms indefinite additive products with ethyl iodide and bromine, but is not attacked by alkaline reducing agents. Oxidation with a very dilute solution of potassium permanganate yields diisopropyl ketone, and an undetermined compound, $C_8H_{14}ON_2$, which is a colourless oil boiling at 245° , together with small quantities of oxalic, α -hydroxyisobutyric, isobutyric, and acetic acids.

Propionaldazine, $N_2(\text{CH}_2\text{Et})_2$, prepared in a similar manner to isobutaldazine, is a clear, mobile liquid boiling at $144\text{--}146^\circ$. *Capronaldazine* is a clear, viscous oil boiling at 246° . These two aldazines, and the dimethyl- and diethyl-ketazines are decomposed in ethereal solution by dry hydrogen chloride, although propionaldazine yields traces of an oil which has a camphor-like odour and may be a pyrazoline derivative.

R. H. P.

Action of Mercury on Methylene Iodide. By VICTOR THOMAS (*Bull. Soc. Chim.*, 1900, [iii], 23, 49—51).—The author confirms Sakurai's statement (*Trans.*, 1880, 37, 658) that the interaction of mercury, methylene iodide, and mercurous iodide in the cold results in the formation of the compound $\text{CH}_2\text{I}_2\text{Hg}$ and other products, but finds that the mercurous iodide plays no part in the reaction, which takes place equally well in the absence of this salt. When mercury is heated with methylene iodide for 10—12 hours in a sealed tube at $190\text{--}200^\circ$, large crystals of mercuric iodide are formed, and on opening the tube a mixture of methane (1 vol.) and ethane (2 vols.) is liberated.

N. L.

Secondary Butylbenzene. By TADEUSZ ESTREICHER (*Ber.*, 1900, 33, 436—443).— β -Chlorobutane boils at 66.5° under 731.8 mm. pressure, has a sp. gr. 0.8948 at 0° , and a critical temperature lying between 246.7° and 248.4° . *sec*-Butylbenzene, prepared from benzene, aluminium chloride, and β -chlorobutane or *sec*-butyl chloride, boils at $173.2\text{--}174.2^\circ$ under 742.4 mm. pressure; on treatment with fuming sulphuric acid, it yields *sec-butylbenzene-p-sulphonic acid*; this forms deliquescent crystals melting at $84\text{--}85^\circ$, yields a *barium* salt crystallising in needles or tablets with $1\frac{1}{2}\text{H}_2\text{O}$, and an easily soluble *potassium* salt crystallising in needles. *p-sec-Butylphenol*, obtained by fusing the sulphonic acid with potash, crystallises in long, silky needles, melts at $53\text{--}54^\circ$, and boils at $239.5\text{--}240.5^\circ$ under 750.6 mm. pressure; its *acetyl* derivative is a clear liquid with an anise-like odour and boils at 255.5° under 743.9 mm. pressure.

R. H. P.

Explanation of the Würtz-Fittig Synthesis. IV. Bromomesitylene and Sodium; Mesityl Bromide and Sodium. By MAX WEILER (*Ber.*, 1900, 33, 334—345. Compare *Abstr.*, 1894, i, 604; 1896, i, 237, 242; 1899, i, 490).—Mesitylene has been employed as a diluent instead of ether or benzene in the reaction between bromomesitylene and sodium with the result that a yield of 14.2 instead of 8.9 per cent. of hydrocarbons containing two mesityl groups has been obtained. This mixture may be separated into 40.8 per cent. of *s*-tetramethyldibenzyl (m. p. 78°), 9.7 per cent. of 3:5:2':4':6'-pentamethyldiphenylmethane (*Abstr.*, 1899, i, 703), 12.6 per cent. of a crystalline mixture of the above, and 29.4 per cent. of a yellow, non-crystallisable oil with a purple fluorescence. Practically the same products are obtained when mesityl bromide is treated with sodium in the presence of mesitylene.

The interpretation previously given is held to cover these new facts, as also that given by Nef (*Annalen*, 1887, 298, 372; 1899, 309, 167). *s*-Tetramethyldibenzyl, the so-called dimesityl (*loc. cit.*), has also been obtained by Moritz and Wolfenstein (*Abstr.*, 1899, i, 910) by the

action of persulphates on mesitylene. On oxidation with chromium trioxide, it does not yield any definite products; with nitric acid, it gives a small amount of mesitylenic acid, and with potassium permanganate trimesic acid. Its constitution follows from the following method of synthesis. *s*-Tetramethylbenzoin is readily obtained by the action of alcoholic potassium cyanide on *s*-dimethylbenzaldehyde; it crystallises in long, yellow plates melting at 93—94°, dissolves readily in most organic solvents, reduces Fehling's solution in the cold, gives a red coloration with ferric chloride and when reduced with hydriodic acid and phosphorus yields *s*-tetramethyldibenzyl together with a substance melting at 72—75°.

When pentamethyldiphenylmethane is brominated in the presence of iodine, it yields a *tetrabromo*-derivative, $C_{18}H_{18}Br_4$, which crystallises from benzene in plates or stout needles melting at 230—232°, and is not decomposed when boiled for 1½ hours with alcoholic potash. When oxidised with chromium trioxide, the hydrocarbon yields a small amount of an acid together with a substance which crystallises in yellow needles, melts at 229—232°, and is probably 1:3:5:7-tetramethylantraquinone. When alkaline permanganate is employed, an acid is obtained which crystallises from hot water in small prisms, sinters at 350—355°, and yields a methyl ester melting at 146—147°. When treated in carbon disulphide solution with chromyl chloride, the hydrocarbon yields a certain amount of mesitoylmesitylene together with other products. Mesitoylmesitylene (Abstr., 1899, i, 704), when treated with zinc and aqueous alcoholic potash by Elbs's method (Abstr., 1886, 461), yields *pentamethylbenzhydrol*, which crystallises in long, stout prisms, melts at 98—99°, and is readily soluble in most organic solvents. It does not react with sodium hydroxide and benzoyl chloride, or with acetic anhydride or phenylcarbimide in the cold; on boiling, the *acetate* melting at 111·5—112, is formed. When reduced with hydriodic acid and phosphorus, it yields pentamethyldiphenylmethane.

J. J. S.

Acetylation with Acetic Anhydride in Aqueous Solution. By JOHANNES PINNOW (*Ber.*, 1900, 33, 417—420).—It is shown that the acetates of aromatic amines in aqueous solution or suspension can be directly acetylated if placed in contact with acetic anhydride. Quantitative experiments with 1 per cent. aniline acetate solutions show that, at any temperature between 20° and 50°, 99 per cent. of the acetic anhydride is converted into acetanilide. An aqueous solution of aniline hydrochloride can be thus acetylated despite the free hydrochloric acid, and even when the latter is considerably in excess (1 mol. aniline to 4 mols. HCl) about 15 per cent. of the anhydride is converted into acetanilide.

R. H. P.

[Acylation] in Presence of Pyridine. By GAETANO MINUNNI (*Gazzetta*, 1899, 29, ii, 443—451).—A historical review of researches on the acetylation and benzylation of hydroxy-, amino-, and imino-compounds in presence of pyridine.

T. H. P.

Nitration of Dimethylaniline dissolved in Concentrated Sulphuric Acid. By PIETER VAN ROMBURGH (*Proc. K. Akad. Wetensch. Amsterdam*, 1899, 2, 342—344).—When dimethylaniline

dissolved in concentrated sulphuric acid is treated with excess of nitric acid, the chief products of reaction are the *m*- and *p*-mononitro-compounds, a small amount of 2:4-dinitrodimethylaniline being simultaneously formed. If the solution be added to a mixture of ice and water, further nitration occurs and the two dinitro-compounds previously described by the author are produced; mononitro-compounds only are obtained when the dilution is effected in the presence of excess of caustic soda. This result is confirmed by direct experiment, the two dinitro-compounds being prepared by nitrating *m*-nitrodimethylaniline in 30 per cent. sulphuric acid. It is probable that, by nitrating dimethylaniline by Groll's method, the meta-compound is exclusively formed in the concentrated sulphuric acid, whilst the para-isomeride is produced after dilution. 2:4-Dinitrodimethylaniline is the sole product of the nitration of *p*-nitrodimethylaniline.

G. T. M.

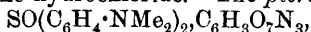
Action of Thionyl Chloride on Dimethylaniline and Diethylaniline. By AUGUST MICHAELIS and P. SCHINDLER (*Annalen*, 1899, 310, 137—155. Compare Abstr., 1893, i, 515).—It has been shown by Michaelis and Godchaux that, when thionyl chloride acts on dimethylaniline dissolved in a small quantity of ether, thiodimethylaniline and dimethylanilinesulphonic chloride are produced.

The compound $2\text{NMe}_2\text{Ph}\cdot\text{SOCl}_2$, obtained on adding thionyl chloride, diluted largely with light petroleum, to a very dilute, ice-cold solution of dimethylaniline (1 mol.) in the same medium, forms dark red, hygroscopic crystals, which become yellow and resinous when exposed to moist air; the colour changes to green at 80° , and the substance melts at 100° . Cold water resolves this compound into dimethylaniline, thiodimethylaniline, sulphur dioxide, a yellow powder of uncertain character having the composition $\text{NMe}_2\text{Ph}\cdot\text{SO}_2$, and dimethylanilinesulphonic acid, $\text{NMe}_2\cdot\text{C}_6\text{H}_4\cdot\text{SO}_2\text{H}$, of which the *sodium* salt crystallises in long needles, and the *potassium* salt in large, rhombic plates.

Dimethylaminophenylethylsulphone, $\text{NMe}_2\cdot\text{C}_6\text{H}_4\cdot\text{SO}_2\text{Et}$, prepared from sodium dimethylanilinesulphinate and ethyl bromide, crystallises from water in lustrous leaflets and melts at 116° ; the *hydrochloride* melts at 139 — 140° .

Dimethylaminophenylmethylsulphone, $\text{NMe}_2\cdot\text{C}_6\text{H}_4\cdot\text{SO}_2\text{Me}$, crystallises from hot water in colourless needles and melts at 166 — 167° .

Thionyl dimethylaniline, $\text{SO}(\text{C}_6\text{H}_4\cdot\text{NMe}_2)_2$, produced by the action of acids on the salts of dimethylanilinesulphonic acid, separates from water in lustrous crystals and melts at 151 — 152° , forming a dark blue liquid; hydrochloric acid resolves it into dimethylaniline and sulphur dioxide, whilst sodium reduces the alcoholic solution to thiodimethylaniline. The *hydrochloride* melts at 174° , and in neutral solution yields the *platinichloride* containing $8\text{H}_2\text{O}$, which decomposes at 50° without melting; the *platinichloride* containing $2\text{H}_2\text{O}$ is obtained on adding platinic chloride to a strongly acid solution of thionyl dimethylaniline hydrochloride. The *picrate*,



melts at 119° , and the *picrate*, $\text{SO}(\text{C}_6\text{H}_4 \cdot \text{NMe}_2)_2 \cdot 2\text{C}_6\text{H}_3\text{O}_7\text{N}_3$, crystallises from hot water in slender needles and melts at $155-156^{\circ}$.

The compound $2\text{NEt}_2\text{Ph} \cdot \text{SOCl}_2$, prepared from diethylaniline and thionyl chloride, forms red crystals, and is converted by water into diethylanilinesulphinic acid, the sodium and potassium salts of which form lustrous, colourless crystals.

Thionyldiethylaniline, $\text{SO}(\text{C}_6\text{H}_4 \cdot \text{NEt}_2)_2$, obtained by the action of boiling water on diethylanilinesulphinic acid, forms small, lustrous crystals, and melts at $128-129^{\circ}$; it yields two *platinichlorides*, containing $8\text{H}_2\text{O}$ and $2\text{H}_2\text{O}$ respectively. M. O. F.

Stereochemical Observations on the Reaction between Picric Chloride and Aromatic Amines. By EDGAR WEDEKIND (*Ber.*, 1900, 33, 426—436. Compare Turpin, *Trans.*, 1891, 59, 714).—It has been shown by Wedekind and Stauwe (*Abstr.*, 1898, i, 192, 573), in studying the influence of the relative positions of substituents on the formation of tetrazolium bases, that the nitro-group forms an exception to the known rules, and therefore the action of picryl chloride on various amines has been studied. Of the various monosubstituted primary amines, the para-compounds form the picryl derivatives most readily, followed by the meta-, and then the ortho-compounds, although there is not much difference between them. The nitro-group again forms an exception, since, for example, *m*-nitraniline forms a picryl derivative with the greatest ease, and *o*-nitraniline only with great difficulty. The stereochemical influence of the ortho-position is strikingly shown by the picrylaminoacetophenones, of which the para-compound easily forms a phenylhydrazone, whilst the ortho-compound will not react with phenylhydrazine.

Secondary amines of the type NHXY (where $\text{X} = \text{Ph}$, $\text{Y} = \text{Me}$, Et , CH_2Ph) or piperidine form normal picryl derivatives; diphenylamine and carbazole, on the other hand, form additive compounds with 2 mols. of picryl chloride, this being probably the first stage of the reaction, of which the completion is hindered by stereochemical causes. Compounds of the phenylenediamine type (even para-compounds) form only mono-picryl derivatives, whilst those of the benzidine series form dipicryl derivatives, which, curiously, are soluble in alkalis and reprecipitated by acids.

The following picryl derivatives were prepared by treating 2 mols. of the amine with 1 mol. of picryl chloride; the melting points are quoted; the figures in brackets give the yield expressed as percentage of that theoretically possible.

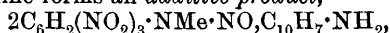
Picrylpiperidine (Turpin, *loc. cit.*), $104-106^{\circ}$, (73.5); *o*-picrylamino-benzoic acid, $271-272^{\circ}$, (84.7); *m*-picrylamino-benzoic acid, $233-234$, (84.7); *p*-picrylamino-benzoic acid, $292-293^{\circ}$, (97.9); *o*-picrylnitro-aniline, 220° , (5.3); *m*-picrylnitroaniline (Austen, *this Journ.*, 1874, 165), $202-203^{\circ}$, (91.2); *p*-picrylnitroaniline (Austen, *loc. cit.*), $214-215^{\circ}$, (80.2); *o*-picrylchloroaniline, $158-159^{\circ}$, (86); *m*-picrylchloroaniline, $137-139^{\circ}$, (88.9); *p*-picrylchloroaniline, $169-170^{\circ}$, (92.5); *p*-picryl-aminoacetophenone, $162-163^{\circ}$, (98.5); *o*-picrylaminoacetophenone, 232° ; *o*-picrylamino-benzaldehyde, $203-205^{\circ}$; *p*-picrylamino-phenol (Turpin, *loc.*

cit.), 172—173°, (97—98); *m*-picrylamino-phenol, 203—204°, (86—88); *p*-picrylaminoacetanilide, 240—242°; picrylmethylaniline (Turpin, *loc. cit.*), 108—110°, (65—70); picrylethylaniline, 105—107°, (50—60).

The *phenylhydrazone* of *p*-picrylaminoacetophenone melts at 218—219°. Diphenylamine forms an additive compound with 2 mols. of picric chloride, which crystallises in lustrous, red tablets melting at 63—64° (compare Turpin, *loc. cit.*). The analogous compound derived from carbazole forms yellowish-red needles melting at 160—165°.

R. H. P.

Nitrosoamines of Methylated Nitroanilines. By EUGEN BAMBERGER and JENS MÜLLER (*Ber.*, 1900, 33, 100—113. Compare *Abstr.*, 1897, i, 241).—*Nitrosomethylpicramide*, $C_6H_2(NO_2)_3 \cdot NMe \cdot NO$, prepared by the action of nitrous fumes on a solution of methylpicramide, crystallises from alcohol in glistening, yellow, rhombic plates or slender needles, and melts at 106·5°; caustic alkalis, methylamine, and ammonia turn the alcoholic solution to a blood-red colour (compare the 'nitroic acids' of Hantzsch and Kissel, this vol., i, 89); unlike *p*-nitromethylanilinenoitrosoamine, it does not liberate diazomethane when boiled with methyl alcoholic potash, and it also differs from nitrosoacetanilide (*loc. cit.*) in that it does not give any trinitrodiphenyl when boiled for two days with dry benzene. When mixed with α -naphthylamine in benzene or alcoholic solution, picrylmethylnitrosoamine forms an *additive product*,



which separates in dark brown to black needles, melts at 120·5—121°, and can be crystallised unchanged from benzene; it is completely dissociated in solution, and the free nitrosoamine can be separated in part by diluting the solution with water; the solution in sulphuric acid is olive-green, but becomes deep red on adding water. When warmed with alcohol, or left in contact with it in the cold for some days, the additive product is converted into picryl- α -naphthylamine, but no diazomethane is produced. The additive product with β -naphthylamine was not separated from the dark brown solution, but was converted directly into *picryl- β -naphthylamine*. This crystallises from acetic acid in glistening, coral-red prisms, with a metallic lustre, and melts at 233—233·5°; it also exists in a second, orange-yellow modification, which melts at the same temperature. Ammonia converts the nitrosoamine into picramide, whilst aniline gives an orange-red picrylaniline, melting at 178—179°, which is probably a second modification of the scarlet-red picrylaniline, melting at 175°, prepared by Clemm from picryl chloride and aniline (*Ber.*, 1870, 3, 126). When heated at 70—80° for several days, the nitrosoamine is partly converted into methylpicramide. The *additive product* of methylpicramide and β -naphthylamine, $C_6H_2(NO_2)_3 \cdot NHMe, C_{10}H_7 \cdot NH_2$, crystallises from alcohol in dark brown needles with a violet shimmer, and melts at 132·5—133°.

An *additive product*, $C_6H_2Cl(NO_2)_3, C_{10}H_7 \cdot NH_2$, separates in brown needles on mixing cold alcoholic solutions of picryl chloride and α -naphthylamine, sinters at 110·5—111·5°, and melts with decomposition at 180°: under other conditions, picrylnaphthylamine is formed directly,

2 : 4-*Dinitrophenylmethylnitrosoamine*, $C_6H_3(NO_2)_2 \cdot NMe \cdot NO$, crystallises from alcohol in pale yellowish needles, melts at $83-84.5^\circ$, and is fairly stable when pure; when boiled with dry benzene, it does not give dinitrodiphenyl, but is partially converted into dinitromethylaniline. By the action of α -naphthylamine on the nitrosoamine, a mixture of aminoazonaphthalene and dinitromethylaniline is produced.

p-Nitrophenylmethylnitrosoamine is not changed by boiling with benzene, and does not convert β -naphthol into the methyl ether; the nitroso-group is very stable, but can be removed by boiling with α -naphthylamine and fusel oil, giving *p*-nitromethylaniline and (apparently) aminoazonaphthalene. T. M. L.

Relation of Fulminic to Isocyanic Acid and the Formation of Phenylurethane from Phenol and Mercuric Fulminate. By ROLAND SCHOLL and F. KACER (*Ber.*, 1900, 33, 51-54. Compare Abstr., 1891, 282).—Phenylurethane, $NH_2 \cdot CO_2Ph$, is formed when mercuric fulminate is moistened with alcohol and added in small portions to phenol heated at $150-160^\circ$. J. J. S.

The Molecular Rearrangement of *o*-Aminophenyl Ethyl Carbonate to α -Hydroxyphenylurethane. By JAMES H. RANSOM (*Amer. Chem. J.*, 1900, 23, 1-50. Compare Abstr., 1898, i, 415).—The substance obtained by reducing *o*-nitrophenyl ethyl carbonate with tin and hydrochloric acid (Bender, Abstr., 1887, 37) is Groenvik's *o*-hydroxyphenylurethane, $OH \cdot C_6H_4 \cdot NH \cdot CO_2Et$ (this Journ., 1877, i, 473), and its formation is therefore due to a migration of the carboxyethyl group; it melts at 86.5° , not 95° as stated by Bender, or 120° by Groenvik.

o-Benzoyloxyphenylurethane, $OBz \cdot C_6H_4 \cdot NH \cdot CO_2Et$, is insoluble in alkalis or acids, and melts at 75.5° ; when distilled, it yields alcohol, ethyl benzoate, benzoylcarbonylaminophenol, benzenylaminophenol, and a substance melting at $85-105^\circ$, probably impure carbonylaminophenol. Benzoylcarbonyl-*o*-aminophenol, $C_6H_4 \begin{smallmatrix} \text{NBz} \\ \diagup \quad \diagdown \\ \text{O} \end{smallmatrix} CO$, is also made by treating carbonylaminophenol in alkaline solution with benzoyl chloride; it melts at 174° .

m-Nitrobenzoyloxyphenylurethane, $NO_2 \cdot C_6H_4 \cdot CO_2 \cdot C_6H_4 \cdot NH \cdot CO_2Et$, is soluble in alcohol, ether, or benzene, insoluble in alkalis and acids, and crystallises from a mixture of benzene and light petroleum in slender prisms melting at 86.5° . On distillation, it yields alcohol, *m*-nitrobenzoic acid and its ethyl ester, carbonylaminophenol, and *m*-nitrobenzenyl-*o*-aminophenol, $C_6H_4 \begin{smallmatrix} \text{N} \\ \diagup \quad \diagdown \\ \text{O} \end{smallmatrix} C \cdot C_6H_4 \cdot NO_2$. This substance is also obtained by heating together *o*-aminophenol and *m*-nitrobenzoyl chloride; it is sparingly soluble in the usual organic media excepting chloroform, and separates from alcohol in greyish-yellow crystals melting at 207° .

m-Nitrobenzoylcarbonylaminophenol is somewhat soluble in acetic acid, readily soluble in chloroform, and melts at $199.5-201.5^\circ$. *m*-Nitrobenzoyl-*o*-aminophenol dissolves in alkalis, forming a bright yellow solution, and crystallises from alcohol in thick prisms melting

at 207°. When treated with ethyl chloroformate and potassium hydroxide, it affords *m*-nitrobenzoylhydroxyphenylurethane.

m-Nitrobenzoyl-*o*-aminophenyl benzoate, $\text{NO}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{CO} \cdot \text{NH} \cdot \text{C}_6\text{H}_4 \cdot \text{OBz}$, separates from alcohol in long, white, hair-like needles, is not very soluble in alcohol, and melts at 151—153°. *Benzoyl-o*-aminophenyl *m*-nitrobenzoate, crystallises in short, thick prisms, and melts at 152°. Both the foregoing substances, on hydrolysis with alkali, yield benzoyl-*o*-aminophenol and *m*-nitrobenzoic acid, but cannot be converted into one another.

Carbethoxyaminophenyl phenylcarbamate,

$\text{NHPh} \cdot \text{CO}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{NH} \cdot \text{CO}_2\text{Et}$, or $\text{NHPh} \cdot \text{CO} \cdot \text{NH} \cdot \text{C}_6\text{H}_4 \cdot \text{O} \cdot \text{CO}_2\text{Et}$, made by treating a solution of hydroxyphenylurethane and phenylcarbimide in absolute ether with aluminium chloride, separates from alcohol in nearly white prisms melting at 116—118°, and is fairly soluble in most of the ordinary media, but insoluble in alkalis or acids.

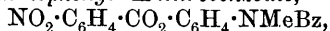
When hydroxydiphenylcarbamide in alkaline solution is treated with ethyl chloroformate, an oil is precipitated which, on hydrolysis, yields hydroxyphenylurethane.

Carbonylmethylaminophenol, $\text{C}_6\text{H}_4 \langle \text{NMe} \rangle_{\text{O}} \text{CO}$, is very soluble in

most organic solvents and melts at 86°. *o*-Methylaminophenol melts at 88—90° (compare Seidel, Abstr., 1891, 53). *Benzoylmethyl-o*-aminophenol, $\text{OH} \cdot \text{C}_6\text{H}_4 \cdot \text{NMeBz}$, melts at 160—162°. *Benzoylmethyl-o*-aminophenyl ethyl carbonate separates from light petroleum in long, silky needles, melts at 68°, and is soluble in alcohol, ether, or benzene; on alkaline hydrolysis, it yields benzoylmethyl-*o*-aminophenol. *o*-Hydroxyphenylmethylurethane, $\text{OH} \cdot \text{C}_6\text{H}_4 \cdot \text{NMe} \cdot \text{CO}_2\text{Et}$, melts at 53°, dissolves in alkalis, and is reprecipitated by acids. *o*-Benzoyloxyphenylmethylurethane, $\text{OBz} \cdot \text{C}_6\text{H}_4 \cdot \text{NMe} \cdot \text{CO}_2\text{Et}$, crystallises in needles, melts at 88—90°, is fairly soluble in most organic media, but insoluble in alkalis or acids.

m-Nitrobenzoylmethyl-*o*-aminophenol, $\text{OH} \cdot \text{C}_6\text{H}_4 \cdot \text{NMe} \cdot \text{CO} \cdot \text{C}_6\text{H}_4 \cdot \text{NO}_2$, separates from alcohol in beautiful, large crystals, melts at 105°, and decomposes at 110—115°; the benzoate, $\text{C}_{21}\text{H}_{16}\text{N}_2\text{O}_2$, melts at 141°.

Benzoylmethyl-o-aminophenyl *m*-nitrobenzoate,



separates from alcohol in large, stout crystals melting at 123·5°.

o-Methoxyphenylurethane, $\text{OMe} \cdot \text{C}_6\text{H}_4 \cdot \text{NH} \cdot \text{CO}_2\text{Et}$, made by the action of ethyl chloroformate on anisidine in presence of alkali, is a nearly colourless oil boiling at 180—182° under 26 mm. pressure; the monobromo-derivative appears to melt at 102·5°, but is mixed with a second substance melting at 252°, from which it is difficult to separate it.

o-Methoxyphenylurethane is converted into *o*-methoxyphenylcarbamide (m.p. 146·5°) on treatment with phosphorus pentachloride and ammonia. *Phenyl-o*-methoxyphenylcarbamide,



separates from a mixture of chloroform and light petroleum in thick prisms, melts at 144°, and is soluble in alcohol, ether, or chloroform.

o-Hydroxyphenylurethane is easily methylated by von Pechmann's method with diazomethane, yielding *o*-methoxyphenylethylurethane.

o-Aminophenyl ethyl carbonate, $\text{NH}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{O} \cdot \text{CO}_2\text{Et}$, made by reducing *o*-nitrophenyl ethyl carbonate with tin and hydrochloric acid at 0° , forms an oil which, when kept over sulphuric acid, changes to *o*-hydroxyphenylurethane. The *hydrochloride*, $\text{C}_9\text{H}_{11}\text{ON}_3 \cdot \text{HCl}$, is a white solid which melts and evolves gas at 150 — 152° , and when heated in aqueous solution deposits hydroxyphenylurethane. The *platinichloride*, $\text{C}_9\text{H}_{11}\text{ON}_3\text{PtCl}_6$, forms yellow crystals. Attempts to prepare a benzoyl derivative of aminophenyl ethyl carbonate resulted in the formation of the benzoyl derivative of hydroxyphenylurethane.

As it was thought that the hydrochloride of ethoxymethenylaminophenol might be formed during the reduction of *o*-nitrophenyl ethyl carbonate, a comparison of ethoxymethenylaminophenol with aminophenyl ethyl carbonate was made; it was found that on passing hydrogen chloride into its solution in absolute ether or light petroleum, ethyl chloride was evolved and carbonylaminophenol was produced, a fact which indicates that the base is not an intermediate product in the formation of *o*-hydroxyphenylurethane.

p-Nitrophenyl ethyl carbonate, made from *p*-nitrophenol or by nitrating phenyl ethyl carbonate, is soluble in light petroleum, ether, or alcohol, and crystallises in long, white needles melting at 68° . *p*-Aminophenyl ethyl carbonate melts at 36° , dissolves in acids, and gives no purple colour with ferric chloride; the *hydrochloride*, $\text{C}_9\text{H}_{11}\text{ON}_3 \cdot \text{HCl}$, darkens at 160° and melts at 197° with violent decomposition; the *platinichloride*, $(\text{C}_9\text{H}_{11}\text{ON}_3)_2 \cdot \text{H}_2\text{PtCl}_6$, is a bright yellow, crystalline solid which blackens at 208° and melts at 237° . *p*-Ureidophenyl ethyl carbonate is insoluble in alkalis and melts at 147 — 150° . All attempts to cause a rearrangement of the molecule of *p*-aminophenyl ethyl carbonate were unsuccessful. A. L.

Oxidation of Aqueous Solutions of Aromatic Hydroxylamines by Atmospheric Oxygen. By EUGEN BAMBERGER (*Ber.*, 1900, 33, 113—122).—The first product of the oxidation of β -phenylhydroxylamine and its substitution products by oxygen in aqueous solution is a nitrosobenzene, which usually combines more or less rapidly with the unchanged phenylhydroxylamine to form an azoxybenzene. In the case of ortho-dimethylated phenylhydroxylamines, such as 2:6-xylylhydroxylamine and 2:4:6-mesitylhydroxylamine, the stable nitroso-compound is the only product, but 2:5-xylylhydroxylamine gives a mixture of nitrosoxylenes and azoxyxylenes; in the case of phenylhydroxylamine itself, the condensation proceeds so rapidly that the presence of nitrosobenzene can only be detected by its characteristic odour.

Hydrogen peroxide is always produced in the oxidation, the actual yield being about 90 per cent. of that required for 1 mol.; the β -substituted hydroxylamines are thus among the substances that bring about the increase in activity ('*Activirung*') of oxygen.

The oxidation proceeds much more rapidly in presence of alkalis, giving rise to the formation of a considerable proportion of nitrobenzene. Similar products are formed in neutral or alkaline solution when the

oxidation is brought about by hydrogen peroxide; this agent has no action on nitrosobenzene in neutral solution, but in alkaline solution readily oxidises it to nitrobenzene; the formation of the latter is therefore probably due to the action of hydrogen peroxide on the nitrosobenzene, which is the first product in both cases.

T. M. L.

Action of Alkalis on Aromatic Hydroxylamines. By EUGEN BAMBERGER and FRIEDRICH BRADY (*Ber.*, 1900, 33, 271—274).—Sodium interacts with phenylhydroxylamine in ethereal solution to form the monosodium derivative, $\text{NHPh}\cdot\text{ONa}$, a white, crystalline powder; Schmidt's disodium derivative (this vol., i, 20), however, could not be obtained. Cold aqueous sodium hydroxide converts phenylhydroxylamine, when air is excluded almost quantitatively into azoxybenzene and aniline, no trace of nitrobenzene being formed; in dilute solution, the action is very slow, but takes place more rapidly on increasing either the concentration or the amount of alkali, whilst if air is present the action is very rapid, azoxybenzene and nitrobenzene being formed. Since *m*-xylyl-2-hydroxylamine is not acted on by aqueous sodium hydroxide when air is excluded, two methyl groups in the ortho-position relatively to the $\text{NH}\cdot\text{OH}$ radicle exercise a shielding influence; when air is present, both *m*-xylyl-2-hydroxylamine and mesitylhydroxylamine yield the corresponding nitroso-compounds. It thus appears that, in the case of phenylhydroxylamine, the azoxybenzene is formed by the interaction of the nitrosobenzene initially produced with the base; with *p*-tolylhydroxylamine, indeed, the formation of nitrosotoluene can be detected.

The action of ethyl alcoholic potassium hydroxide in absence of air on phenylhydroxylamine gives, after 10 days, a quantitative yield of azobenzene; with methyl alcohol, the action is similar, but traces of aniline and nitrobenzene are also formed.

W. A. D.

Aromatic Nitro-derivatives. By ANGELO ANGELI and FRANCESCO ANGELICO (*Realt. Accad. dei Lincei*, 1899, [v], 8, ii, 28—32).—Whilst substituted hydroxylamines having the substituent in the amino-group react with nitro-compounds with the formation of substances containing the complex $\cdot\text{NO}:\text{N}\cdot\text{OH}$, with those in which the substitution is in the hydroxy-group of the hydroxylamine no such reaction takes place. The nature and position of the substituent radicle also influence the nature of the product obtained. Thus, nitrobenzene and *p*-nitrotoluene give rise to the compounds $\text{Ph}\cdot\text{NO}:\text{N}\cdot\text{OH}$ and $\text{C}_6\text{H}_4\text{Me}\cdot\text{NO}:\text{N}\cdot\text{OH}$ respectively. α -Nitronaphthalene, however, yields, with hydroxylamine, 1 : 4-nitronaphthylamine.

When *p*-nitrotoluene reacts with amyl nitrite in presence of sodium ethoxide, the side chain of the toluene is attacked and *p*-nitrobenzaldehyde formed.

T. H. P.

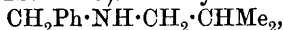
Action of Sodium and Amyl Alcohol on Phenylaminoacetic Acid. By ALFRED EINHORN and HERMANN PFEIFFER (*Annalen*, 1899, 310, 218—225. Compare *Abstr.*, 1896, i, 551).—*Phenylisoamylaminoacetic acid*, $\text{C}_5\text{H}_{11}\cdot\text{NH}\cdot\text{CHPh}\cdot\text{CO}_2\text{H}$, produced on adding sodium to a boiling solution of phenylaminoacetic acid in amyl alcohol, separates from acetic acid as a microcrystalline powder and decom-

poses at 252° ; the *nitroso*-derivative crystallises from water in slender white needles and melts at 109° .

Benzylisoamylamine, $\text{CH}_2\text{Ph}\cdot\text{NH}\cdot\text{C}_5\text{H}_{11}$, prepared by heating the foregoing acid, is a colourless oil which boils at $236\text{--}239^{\circ}$ under 720 mm. pressure; the *hydrochloride*, *platinichloride*, and *aurichloride* melt at 253° , 203° , and 190° respectively. *Catecholcarbобензылісоамыламіне*, $\text{OH}\cdot\text{C}_6\text{H}_4\cdot\text{O}\cdot\text{CO}\cdot\text{N}(\text{C}_5\text{H}_{11})\cdot\text{CH}_2\text{Ph}$, obtained by the action of catechyl carbonate (compare Abstr., 1898, i, 409), crystallises from petroleum in cubes and melts at 74° . Benzylisoamylamine is identical with the base described by Zaunschirm (Abstr., 1888, 1077.)

The *acid*, $\text{C}_8\text{H}_{14}\text{O}_3$, another product of the action of sodium and amyl alcohol on phenylaminoacetic acid, crystallises in white needles and melts at 133° ; the *calcium* salt is microcrystalline. M. O. F.

Benzylbutylamines. By ALFRED EINHORN and HERMANN PFEIFFER (*Annalen*, 1899, 310, 225—229).—Benzylisobutylamine,



has been already described by Zaunschirm (Abstr., 1888, 1077); the *hydrochloride* and *aurichloride* melt at 175° and 190° respectively.

Benzyl-n-butylamine, $\text{CH}_2\text{Ph}\cdot\text{NH}\cdot\text{CH}_2\text{Pr}$, prepared by reducing benzylidenebutylamine in alcoholic solution with sodium amalgam, boils at $226\text{--}230^{\circ}$ under 715 mm. pressure; the *hydrochloride*, *aurichloride*, and *platinichloride* melt at 241° , 155° , and 90° respectively.

Benzyl-sec-butylamine, $\text{CH}_2\text{Ph}\cdot\text{NH}\cdot\text{CHMeEt}$, obtained from secondary butylamine by the same process, boils at $218\text{--}225^{\circ}$; the *hydrochloride* and *aurichloride* melt at 180° and 185° respectively.

Benzyl-tert-butylamine, $\text{CH}_2\text{Ph}\cdot\text{NH}\cdot\text{CMe}_3$, obtained by the action of trimethylcarbinyl iodide on benzylamine, is a colourless oil; the *hydrochloride*, *platinichloride*, and *aurichloride* melt at 228° , 221° , and 225° respectively. M. O. F.

Action of Formaldehyde on o-Nitroaniline. By JACOB MEYER and MARTIN ROHMER (*Ber.*, 1900, 33, 250—262. Compare Abstr., 1892, 1450, and 1893, i, 389).—*Anhydro-m-nitro-p-aminobenzyl alcohol*,

$(\text{NO}_2\cdot\text{C}_6\text{H}_3\langle\text{CH}_2\text{NH}\rangle_x)$, is obtained in the form of its hydrochloride either by digesting methylenedi-o-nitraniline with concentrated hydrochloric acid at 40° for 1 hour or by warming a mixture of o-nitroaniline, formaldehyde, and hydrochloric acid; the base is produced by digesting its salt with hot water; it is insoluble in all the low boiling point solvents and in dilute acids, dissolves to a slight extent in aniline, quinoline, or pyridine, nitrobenzene, and separates from solution in reddish-brown nodules melting and decomposing at $265\text{--}270^{\circ}$. In the above experiment, when the digestion with hydrochloric acid is continued for a longer time at the temperature of the water-bath, the filtrate from the insoluble hydrochloride of the anhydro-compound gradually deposits the hydrochloride of 3:3'-dinitro-4:4'-diaminodiphenylmethane; the base obtained by treating this salt with hot water is extremely insoluble in the ordinary solvents, but dissolves more readily in hot nitrobenzene or phenol, and crystallises in red needles melting at $228\text{--}230^{\circ}$; the substance when pure is quite insoluble in hydro-

chloric acid. Gram (Abstr., 1892, 618), who first studied this compound, gave its melting point as 224° , and stated that it dissolved in 20 per cent. hydrochloric acid. The diacetyl derivative melts at $259-260^{\circ}$.

m-Nitro-*p*-aminobenzyl alcohol, $\text{NO}_2 \cdot \text{C}_6\text{H}_3(\text{NH}_2) \cdot \text{CH}_2 \cdot \text{OH}$, is obtained as an amorphous yellow precipitate when a solution of the corresponding anhydro-compound in concentrated sulphuric acid is diluted with water; it melts indefinitely, sintering at 130° and decomposing at 180° ; when dried in a vacuum or when heated with acetic acid, it is reconverted into the anhydride. Tolylenediamine, $[\text{Me} : (\text{NH}_2)_2 = 1 : 3 : 4]$, is ultimately obtained by reducing *m*-nitro-*p*-aminobenzyl alcohol with tin and hydrochloric acid, but when less of these reagents is employed an amorphous base, $\text{NH}_2 \cdot \text{C}_6\text{H}_3 \begin{smallmatrix} \text{NH} \\ \diagup \text{CH}_2 \end{smallmatrix}$ (?), is formed as an intermediate product.

3 : 4 : 3' : 4'-Tetraminodiphenylmethane, obtained by reducing 3 : 3'-dinitro-4 : 4'-diaminodiphenylmethane with tin and hydrochloric acid, crystallises from water in colourless, rhombic leaflets which darken on exposure to air and melt at $137-138^{\circ}$; its salts are all extremely soluble, the solution of the hydrochloride developing a dark red coloration with ferric chloride. The authors cannot corroborate Gram's statement that the base is sparingly soluble in water, and that it yields a platinichloride crystallising in yellow needles.

The *di*-2-methylbenziminazole, produced by heating the tetramino-base with glacial acetic acid, contains 1 mol. of water and has the composition $\text{C}_{17}\text{H}_{18}\text{ON}_4$; the water is not removed by treating the substance with concentrated sulphuric acid, acetic anhydride, or phosphorus oxychloride; it melts at 285° and when heated at this temperature for some time a portion of the water is driven off. The *platinichloride* crystallises in yellow needles which retain the mol. of water even when dried at 100° , the composition of the salt being expressed by $\text{C}_{17}\text{H}_{18}\text{ON}_4 \cdot \text{H}_2\text{PtCl}_6$. The *nitrate*, $\text{C}_{17}\text{H}_{18}\text{O}_6\text{N}_6$, however, corresponds with the anhydrous iminazole; it decomposes at 220° .

The *diiminazole*, $\text{CH}_2(\text{C}_6\text{H}_3 \begin{smallmatrix} \text{N} \\ \diagup \text{NH} \end{smallmatrix} \text{CH})_2$, which results from the action of formic acid on the tetramine, crystallises from alcohol in colourless, oval leaflets and melts at 212° ; it is very hygroscopic. The *nitrate*, $\text{C}_{15}\text{H}_{14}\text{O}_6\text{N}_6$, crystallises in needles melting at 230° ; the *platinichloride*, $\text{C}_{15}\text{H}_{14}\text{ON}_4 \cdot \text{H}_2\text{PtCl}_6$, contains one molecular proportion of water.

The *di*-2-ethylbenziminazole, $\text{CH}_2(\text{C}_6\text{H}_3 \begin{smallmatrix} \text{N} \\ \diagup \text{NH} \end{smallmatrix} \text{C}_2\text{H}_5)_2$, prepared by heating the tetramine with propionic acid, crystallises from dilute alcohol in colourless prisms and melts at $263-264^{\circ}$. The *nitrate* crystallises in colourless needles and melts at 212° ; the *platinichloride* separates in sparingly soluble, pale yellow, prismatic crystals.

The *diazimide*, $\text{CH}_2(\text{C}_6\text{H}_3 \begin{smallmatrix} \text{N} \\ \diagup \text{NH} \end{smallmatrix} \text{N})_2$, obtained by treating a solution of the tetramine in dilute sulphuric acid with sodium nitrite (2 mols.), crystallises in aggregates of needles and melts at 155° ; it

dissolves in sodium hydroxide solution and is reprecipitated by cold dilute acids; it is, however, soluble in hot acids.

The *tetraphenyldiquinoxaline*, $\text{CH}_2(\text{C}_6\text{H}_3 \begin{smallmatrix} \text{N}:\text{CPh} \\ \text{N}:\text{CPh} \end{smallmatrix})_2$, prepared by condensing the tetramine with benzil in alcoholic solution, crystallises from alcoholic chloroform or phenol in clusters of colourless needles and melts at $245\text{--}247^\circ$; it gives the reactions of quinoxaline bases, developing a red coloration on treatment with a mixture of concentrated hydrochloric and sulphuric acids. G. T. M.

Formation of Quaternary Ammonium Compounds in the case of Homologues of Aniline. By EMIL FISCHER and ADOLF WINDAUS (*Ber.*, 1900, **33**, 345—352).—Von Hofmann observed (this Journal, 1872, 1021) that the dimethyl derivatives of mesidine and pentamethylaminobenzene do not yield quaternary ammonium iodides when heated with methyl iodide at 150° . As a result of examining the six isomeric xylidines, the authors find that 1-amino-2:6-dimethylbenzene is the only member of this class which does not give rise to a quaternary ammonium iodide when the dimethyl base is heated with methyl iodide at 100° ; the immediate neighbourhood of a single methyl group suffices to retard the formation of the quaternary ammonium salt. These phenomena are of the same order as those observed by Victor Meyer in connection with the formation of aromatic esters.

The *methiodide* of dimethyl-*as-m*-xylidine melts and decomposes at 183° (186° corr.); the *methochloride* is hygroscopic, and forms a *platinichloride* which crystallises in small rhombs. The *methiodide* of dimethyl-*p*-xylidine crystallises from alcohol in small prisms, and decomposes at $215\text{--}218^\circ$ ($219\text{--}222^\circ$ corr.); the *platinichloride* dissolves sparingly in water. The *methiodide* of dimethyl-*as-o*-xylidine crystallises from water in long, colourless prisms, and decomposes at $235\text{--}237^\circ$ ($240\text{--}242^\circ$ corr.). M. O. F.

Transformation of Phenyl, *p*-Tolyl, and Thymyl Acetates into the corresponding Benzoates. By F. BODROUX (*Bull. Soc. Chim.*, 1900, [iii], **23**, 54—55).—When phenyl acetate is left in contact with zinc dust and benzoyl chloride at the ordinary temperature, heat is developed, hydrogen chloride evolved, and phenyl benzoate formed in almost the theoretical quantity. *p*-Tolyl and thymyl acetates behave in a similar manner, but the reaction does not occur with β -naphthyl acetate. N. L.

Synthetical Preparation of Iretol and allied Phentretol Derivatives. By EMIL KOHNER (*Monatsh.*, 1899, **20**, 926—941).—The author has studied the action of water on derivatives of triaminophenol in order to compare it with the action of water on triaminobenzenes (Weidel, Abstr., 1898, i, 578 *et seq.*).

2:4:6-Triaminophenol, on treatment with water, yields a small quantity of a substance free from nitrogen, which melts at 164° , and may be phentretol (Oettinger, Abstr., 1895, i, 457). The small yield being probably due to the formation of substances of a quinonoid nature as owing to the presence of a NH_2 group in the para-position to an OH group, the alkyl derivatives of picric acid were reduced.

2 : 4 : 6-Trinitromethoxybenzene, on reduction with tin and hydrochloric acid, at a temperature under 75° yields the *dihydrochloride* of diaminohydroxymethoxybenzene, which forms almost colourless needles and gives no coloration with ferric chloride; it forms a *triacetyl* derivative, $\text{OMe} \cdot \text{C}_6\text{H}_2(\text{OAc})(\text{NHAc})_2$, which crystallises in colourless needles melting at $194\text{--}196^{\circ}$. On treating the dihydrochloride with water containing a little stannous chloride in an atmosphere of carbon dioxide, iretol is obtained. Iretole (de Laire and Tiemann, Abstr., 1894, i, 47) forms a *triacetyl* derivative, which crystallises in needles, melts at 49° , and boils at 230° under 25 mm. pressure.

2 : 4 : 6-Trinitroethoxybenzene, on reduction with tin and hydrochloric acid, yields the *dihydrochloride* of diaminohydroxyethoxybenzene, which crystallises with $2\text{H}_2\text{O}$, gives no coloration with ferric chloride or ammonia, and on treatment with water yields 1 : 2 : 4 : 6-*phenetetrol ethyl ether*, which crystallises from water in colourless needles melting at 220° . The latter forms a *triacetyl* derivative which melts at 74° and boils at 232° under 17 mm. pressure. R. H. P.

Bromination of Phenols. By Hugo Ditz (*Zeit. angew. Chem.*, 1899, 1155—1156).—A reply to Vaubel (this vol., ii, 112). The author discusses the fact that tribromo-*m*-cresol bromide is easily reduced by potassium iodide, although dibromo-*o*- and -*p*-cresol bromides are acted on only with difficulty, but no new facts are adduced. W. A. D.

A Condensation Product of Trimethylphloroglucinol. By JAROSLAV ČEČELSKÝ (*Monatsh.*, 1899, 20, 779—791).—*Cedron*, $\text{C}_{16}\text{H}_{18}\text{O}_6$ or $\text{C}_{14}\text{H}_{16}\text{O}_5$, the solid product which separates when aqueous ferric chloride is added to an alcoholic solution of trimethylphloroglucinol (compare Weidel and Wenzel, *Monatsh.*, 1898, 19, 249—267, and Böhm, *Annalen*, 1898, 302, 184), crystallises in aggregates of white, lustreless prisms melting and decomposing at 305° (uncorr.), is insoluble in water and ordinary solvents, except at their boiling point, but soluble in dilute alkalis. It is acid to phenolphthalein, and gives a colour reaction with ferric chloride. Although the formula $\text{C}_{14}\text{H}_{16}\text{O}_5$ is indicated by a cryoscopic determination of the molecular weight, $\text{C}_{16}\text{H}_{18}\text{O}_6$ is adopted, as it alone agrees with that of the derivatives. The *potassium* compound, $\text{C}_{16}\text{H}_{15}\text{O}_6\text{K}_3 \cdot 6\text{H}_2\text{O}$, separates from aqueous solution in well formed, colourless crystals, which rapidly become opaque in the air. *Cedron methyl ether*, $\text{C}_{16}\text{H}_{17}\text{MeO}_6$, crystallises from methyl alcohol in white needles melting at 298° (uncorr.), is soluble in acetic acid, benzene, or dilute alkalis, but practically insoluble in water.

Acetylcedron, $\text{C}_{16}\text{H}_{17}\text{AcO}_6$, crystallises from ethyl acetate as small, lustrous prisms, melts at 260° (uncorr.), and dissolves with ease only in ethyl acetate and acetic anhydride. *Cedron* does not react with phenylhydrazine, is entirely destroyed by oxidising agents, and if fused with caustic alkali is nearly completely oxidised, only a small quantity of fatty acids (acetic and butyric) being obtained. When heated with hydriodic acid under pressure, an oily compound, $\text{C}_8\text{H}_{12}\text{O}_3$, or probably $\text{C}_{16}\text{H}_{24}\text{O}_6$, is obtained; this becomes crystalline after a time, boils at $201\text{--}203^{\circ}$ under 16 mm. pressure, is slightly soluble in water and warm alkali, and has the odour of cedar-wood, whence the

name for the parent substance. When distilled with zinc dust, cedron forms an oil with the odour and boiling point (132°) of mesityl oxide, but dissimilar in composition; other products of a resinous nature are also obtained.

R. L. J.

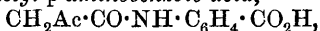
Action of Sodium Mono- and Di-sulphides on Aromatic Nitro-compounds. By J. J. BLANKSMA (*Proc. K. Akad. Wetensch. Amsterdam*, 1899, 2, 271—272).—*o*-Dinitrodiphenyl disulphide, $S_2(C_6H_4 \cdot NO_2)_2$, is obtained by the action of sodium disulphide on *o*-dinitrobenzene; similarly, *o*-dinitrodiphenyl sulphide is produced by the action of sodium monosulphide. The aromatic monosulphide oxidises to a sulphoxide, and then to a sulphone, whilst the disulphide yields 2 mols. of *o*-nitrobenzenesulphonic acid. By the action of sodium disulphide on *p*-chloronitrobenzene, *p*-nitrodiphenyl disulphide is produced. The sulphides of sodium reduce *p*-dinitrobenzene to *p*-dinitroazoxybenzene, a small amount of *p*-nitrothiophenol being formed at the same time. Oxidising agents convert *p*-nitrodiphenyl disulphide into *p*-nitrobenzenesulphonic acid.

G. T. M.

Acidimetry. By HENRI IMBERT and A. ASTRUC (*Compt. rend.*, 1900, 130, 35—37).—The authors have endeavoured to obtain information as to the relative energy of the acidic functions of various acids, hydroxy-acids, phenols, and their substitution derivatives by means of their reactions with helianthin (*H*), phenolphthalein (*P*), and Poirrier's blue (*B*) respectively. Phenol is neutral to *H* and *P* and monobasic to *B*, whereas trinitrophenol is monobasic with all three. The ordinary monobasic acids are acid to *H* and monobasic with *P* and *B*. It is noteworthy that the heat of neutralisation of trinitrophenol is practically identical with that of the monobasic acids. The bromobenzoic acids are monobasic with *P* and *B*, but only the ortho-derivative is acid to *H*, and the nitrobenzoic acids behave in the same way. Glycollic and lactic acids are monobasic with *P* and *B* and acid to *H*. *o*-Hydroxybenzoic acid is monobasic with all three indicators, but the meta- and para-derivatives, although acid to *H*, cannot be accurately estimated with that indicator, whilst, on the other hand, the para-derivative is dibasic with *B*, and the meta-derivative somewhat more than monobasic. Protocatechuic and vanillic acids are monobasic with *P* and dibasic with *B*. Aminoacetic acid is neutral to *H* and *P*, but acid, although not definitely monobasic, with *B*, the presence of the amino-group reducing the energy of the acidic function. *o*- and *m*-Aminobenzoic acids are likewise almost neutral to *H*, whilst the para-derivative is acid, the amino-group in the para-position having little effect on the energy of the acidic function; all three are monobasic with *P* and *B*.

C. H. B.

Action of Ethyl Acetoacetate and Substituted Acetoacetates on *p*-Aminobenzoic Acid in Presence and Absence of Pyridine. By JULIUS TROEGER (*J. pr. Chem.*, 1899, [ii], 60, 507—519).—*Acetoacetyl-p-aminobenzoic acid*,



prepared by heating *p*-aminobenzoic acid with excess of ethyl acetoacetate, crystallises from acetic acid in pale yellow, lustrous needles, melts

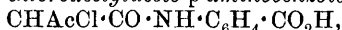
at 190°, and is easily soluble in hot water, hot acetic acid, or cold methyl alcohol.

When *p*-aminobenzoic acid and ethyl acetoacetate are heated together in the presence of a little pyridine, a yellowish-white compound, $C_{18}H_{16}O_5N_2$, separates, which does not melt, and is almost insoluble in the usual solvents; it probably has the constitution



Methylacetoacetyl-p-aminobenzoic acid, $CHMeAc \cdot CO \cdot NH \cdot C_6H_4 \cdot CO_2H$, obtained by heating *p*-aminobenzoic acid with ethyl methylacetoacetate, separates from hot water in pale yellow, silky crystals, and melts at 195—196°; the yield is small; if, however, a little pyridine is present, this substance is not formed, but *p*-carbodibenzamic acid is produced. The latter also results from the action of ethyl ethylacetoacetate on *p*-aminobenzoic acid under similar conditions, but in the absence of pyridine no condensation occurs.

When *p*-aminobenzoic acid is heated with excess of ethyl chloroacetoacetate on the water-bath for 1—2 hours only, and the product treated with alcohol, *chloroacetylaceto-p-aminobenzoic acid*,



separates from the alcoholic solution in well-formed crystals; it melts at 189°, and is insoluble in water; if, however, the heating on the water-bath is prolonged, *hydroxyacetoacetyl-p-aminobenzoic acid* is obtained; this is a yellow substance, which melts at 185°, and is soluble in ethyl acetate. The sodium and silver salts were prepared.

E. G.

Reduction of Benzylaminecarboxylic [Aminophenylacetic] Acids. By ALFRED EINHORN (*Annalen*, 1899, 310, 189—194. Compare Abstr., 1899, i, 407).—Introductory to the abstracts following, and this vol., i, 221, 222.

M. O. F.

Reduction of *p*-Benzylaminecarboxylic Acid. By ALFRED EINHORN and CARL LADISCH (*Annalen*, 1899, 310, 194—204).—

β-Hexahydro-*p*-benzylaminecarboxylic acid, $C_6H_{10} \begin{matrix} CH_2 \cdot NH_3 \\ \diagup \quad \diagdown \\ CO \quad O \end{matrix}$, prepared

by reducing *p*-benzylaminecarboxylic acid with sodium and amyl alcohol, crystallises from acetone in small, hygroscopic cubes, and blackens between 220° and 229°, when it evolves gas; when exposed to air during a few minutes, it absorbs moisture, and then melts at 50—78°. It dissolves readily in organic media, but is insoluble in potash, being probably a betaine. The *hydrochloride* and *hydrobromide* are crystalline, and the *hydriodide* contains $2H_2O$, which is liberated at 160°. The *platinichloride* crystallises from water in orange plates, and melts, evolving gas, at 234°; the *aurichloride* forms needles, which melt and decompose at 208—223°.

α-Hexahydro-*p*-benzylaminecarboxylic acid, $NH_2 \cdot CH_2 \cdot C_6H_{10} \cdot CO_2H$, also obtained on reducing *p*-benzylaminecarboxylic acid, is separated from the foregoing substance by taking advantage of the solubility of its hydrochloride in methyl alcohol; it dissolves in alkalis, crystallises from acetone in cubes, and softens at 270°, but does not melt at 280°. The *hydrochloride* crystallises in leaflets and melts at 260°, which is also the melting point of the *platinichloride*; the *aurichloride* crystallises

from hot water, and melts and decomposes at 150—160°. The methylic salt yields a *hydrochloride* which separates from ethyl acetate in somewhat indefinite crystals, and melts at 195—200°. The *benzoyl* derivative crystallises from alcohol in long needles, and melts at 177—178°, when it decomposes.

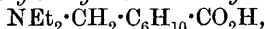
When β -hexahydro-*p*-benzylaminecarboxylic acid is heated with sodium amyloxide in amyl alcohol during 12 hours, it is converted into the α -modification. Nitrous acid gives rise to the *compound*, $C_8H_{14}O_3N_2$, which crystallises from water in prismatic needles and melts at 183°, when it decomposes; it does not give Liebermann's reaction for nitroso-compounds.

The *compound*, $C_{16}H_{26}O_4$, obtained by reducing *p*-methylolbenzoic acid with sodium and amyl alcohol, is insoluble in acetone, chloroform, and benzene; it melts indefinitely at 140—147°.

M. O. F.

Reduction of *p*-Diethylbenzylaminecarboxylic [*p*-Diethylaminophenylacetic] Acid. By ALFRED EINHORN and STAVROS C. PAPASTAVROS (*Annalen*, 1899, 310, 205—217. Compare Friedländer and Mosezyk, *Abstr.*, 1895, i, 414; also Einhorn, *Abstr.*, 1896, i, 551).—*Ethyl ω -chloro-*p*-toluate* boils at 260—280°. When its alcoholic solution is heated with diethylamine *ethyl p*-diethylbenzylaminecarboxylate, $NEt_2 \cdot CH_2 \cdot C_6H_4 \cdot CO_2Et$, is produced, forming a colourless oil which boils at 277—280°; the *hydrochloride* crystallises from absolute alcohol in slender, white needles, and melts at 210°, the *platinichloride* and *aurichloride* melting at 213° and 134° respectively. *p*-Diethylbenzylaminecarboxylic acid crystallises from a mixture of alcohol and benzene, and melts at 150°; the *hydrochloride* contains $2H_2O$, and melts at 185°, whilst the *platinichloride*, *aurichloride*, and *picrate* melt at 202—203°, 156°, and 174—176° respectively. The *amide* melts at 152°, and forms the crystalline *hydrochloride* which melts at 208°. Nitro-*p*-diethylbenzylaminecarboxylic acid *hydrochloride*, $NEt_2 \cdot CH_2 \cdot C_6H_3(NO_2) \cdot CO_2H \cdot HCl$, prepared by the action of diethylamine on the nitro-derivative of ω -chloro-*p*-toluic acid, crystallises from alcohol in small prisms and melts at 225°.

trans-Hexahydro-*p*-diethylbenzylaminecarboxylic acid,



obtained by reducing *p*-diethylbenzylaminecarboxylic acid with sodium in amyl alcohol, melts indefinitely at 85—90°; the *hydrochloride* and *aurichloride* melt at 195° and 153° respectively, and the *picrate* melts at 163—164°.

cis-Hexahydro-*p*-diethylbenzylaminecarboxylic acid, another product of the reduction of *p*-diethylbenzylaminecarboxylic acid, has probably the betaine-like constitution, $C_6H_{10} \begin{matrix} \nearrow CH_2 \cdot NHEt_2 \\ \searrow CO-O \end{matrix}$; it is obtained from the *trans*-modification by the action of sodium amyloxide in hot amyl alcohol; it is a colourless oil with a stupefying odour, and boils at 275—280°; the *hydrochloride* and *picrate* melt at 166° and 163° respectively, and the *aurichloride* crystallises in golden-yellow, prismatic needles. The *ethyl* ester is an oil, and the *methylammonium hydroxide*, $C_{13}H_{27}O_3N$, crystallises from alcohol and ethyl acetate in

needles melting at 142° ; when the latter is heated with concentrated potassium hydroxide, the unsaturated acid, $C_8H_{10}O_2$, is produced, crystallising from petroleum in needles which melt at 164° . M O. F.

Phenylisobutyric and Tolylisobutyric Acids. By OTTO WALLACH (*Chem. Centr.*, 1899, ii, 1047—1048; from *Nachr. k. Ges. Wiss. Göttingen*, 1899, No. 2).—*α-Phenylisobutyric acid*, $CMe_2Ph \cdot CO_2H$, prepared by the action of aluminium bromide on *α*-bromoisobutyric acid and benzene, melts at $77-78^{\circ}$, boils at $150-155^{\circ}$ under 10 mm. pressure, and forms an insoluble silver salt and a calcium salt which crystallises with $2H_2O$. The *methyl* ester boils at 225° , the *ethyl* ester at $235-236^{\circ}$, the *propyl* ester at 250° , and the *butyl* ester at $260-261^{\circ}$. The *chloride* boils at 109° under 13 mm. pressure; the *amide* melts at $160-161^{\circ}$, boils at $200-205^{\circ}$ under 80 mm. pressure, and is almost insoluble in water and only very slightly soluble in ether. *Phenylisobutyronitrile*, $CMe_2Ph \cdot CN$, obtained by the action of phosphorus pentachloride on the amide, boils at 232° , has a sp. gr. 0.966 at 21° , and a specific refractive index n_D 1.50665. By the action of phosphoric oxide on the amide, a hydrocarbon is formed which is probably *diphenyltetramethylethane*, $CMe_2Ph \cdot CMe_2Ph$; it melts at $55-56^{\circ}$, and boils at $138-140^{\circ}$ under 15 mm. pressure. *Phenylisobutylamine*, $CMe_2Ph \cdot CH_2 \cdot NH_2$, prepared by reducing the nitrile, is a colourless oil, and forms a hydrochloride which is very easily soluble in water. The *carbamide*, $CMe_2Ph \cdot CH_2 \cdot NH \cdot CO \cdot NH_2$, obtained by the action of potassium cyanate on the hydrochloride, crystallises in transparent plates and melts at $140-141^{\circ}$.

p-Tolylisobutyric acid, $C_6H_4Me \cdot CMe_2 \cdot CO_2H$, prepared in a similar manner to phenylisobutyric acid, melts at 72° , and boils at $172-180^{\circ}$ under 12 mm. pressure. The *amide* melts at $123-124^{\circ}$, and boils at $240-247^{\circ}$ under 84 mm. pressure. *p-Tolylisobutyronitrile* boils at $247-248^{\circ}$, has a sp. gr. 0.955 at 20° , a specific refractive index n_D 1.5057, and by the action of phosphoric oxide yields *p*-isobutyltoluene. E. W. W.

Chlorylphthalimide and Bromylphthalimide and their Conversion into Isatoic Anhydride and Acetylanthranil. By JULIUS BREDT and H. HOF (*Ber.*, 1900, 33, 21—29).—*Bromylphthalimide*, $C_6H_4 \begin{smallmatrix} \diagup CO \\ \diagdown CO \end{smallmatrix} NBr$, is obtained by running a solution of phthalimide in a slight excess of dilute aqueous sodium hydroxide into a mixture of bromine and water; *chlorylphthalimide*, by adding the first solution gradually to water through which chlorine, kept constantly in excess, is being passed; all solutions are kept at 0° . The two substances melt at $206-207^{\circ}$ and $183-185^{\circ}$ respectively; they lose their halogen readily, forming hypochlorous or hypobromous acid, or derivatives of these. When allowed to remain in dilute alcoholic solution with sodium methoxide or ethoxide, at first at 0° , they yield *dimethyl* and *diethyl carboxyanthranilates* (isatoates), which melt at $60-61^{\circ}$ and $43-44^{\circ}$ respectively, and boil, the first at $165-166^{\circ}$ under 12 mm., the second at 174° under 10 mm. pressure. When a concentrated sodium methoxide solution is employed, a carbamide derivative, $CO(NH \cdot CO \cdot C_6H_4 \cdot CO_2Me)_2$, is the chief product; it melts

and decomposes at 142—143°, and crystallises with chloroform. The diethyl ester, when allowed to remain with a suitable quantity of sodium ethoxide in alcoholic solution, yields ethyl hydrogen carboxy-anthranilate, $\text{CO}_2\text{H}\cdot\text{C}_6\text{H}_4\cdot\text{NH}\cdot\text{CO}_2\text{Et}$, which melts and decomposes at 126°. When this is boiled with acetic anhydride, it yields *acetyl-anthranil*, $\text{C}_6\text{H}_4\cdot\text{N}\begin{smallmatrix} \text{Ac} \\ \diagup \\ \text{CO} \end{smallmatrix}$, which melts at 79—80°, boils at 148—149° under 13 mm. pressure, and yields acetylanthranilic acid when boiled with water. If acetyl chloride is employed instead of acetic anhydride, the product is isatoic anhydride, $\text{C}_6\text{H}_4\cdot\text{N}\begin{smallmatrix} \text{NH}\cdot\text{CO} \\ \diagup \quad \diagdown \\ \text{CO} \end{smallmatrix}\text{O}$, in good yield (compare Erdmann, Abstr., 1899, i, 939). This forms monoclinic plates [$a : b : c = 0.7029 : 1 : 0.6797$; $\beta = 86^\circ 25'$]; when it is heated with alcoholic sodium alkoxides, alkyl anthranilates are formed and other products in addition; the *isobutyl* and *amyl* esters boil respectively at 156—157° and 169—170° under 13½ mm. pressure. C. F. B.

Formation of Indigo from Woad (*Isatis tinctoria*). By MARTINUS W. BEIJERINCK (*Proc. k. Akad. Wetensch. Amsterdam*, 1899, 2, 120—129).—*Indigofera leptostachya* and *Polygonum tinctorium* contain indican; woad, on the other hand, contains free indoxyl. The extraction of woad must be carried out in the absence of air owing to the unstable nature of the indoxyl; hot and cold extracts of the plant both contain this compound. The indoxyl solution obtained either from the indican plants by the action of an enzyme or from woad, is fluorescent and slightly acid; a film of indigotin is slowly produced on its surface, the oxidation being accelerated by alkalis, and to a less extent by acids. Hydrogen peroxide destroys indoxyl, but without forming coloured products. A precipitate of indigo-red is produced by warming an acid or alkaline solution of indoxyl with isatin; a similar result is obtained with an acid solution of indican, and the reaction may be employed in estimating the glucoside. The indigo from woad contains a small quantity of indigo-red. The indigo plants do not appear to contain an oxydase capable of converting indoxyl into indigotin, and this pigment is not produced in their tissues when they are suddenly killed. A large amount of colouring matter, however, is formed when the plants are allowed to die slowly, and the author supposes the oxidation to be due to the formation of alkali in the dying tissues.

When the “indican plants” are asphyxiated at the ordinary temperature by immersion in mercury or exposure to hydrogen or carbon dioxide, the indigo enzyme converts the indican into indoxyl; these dead plants then resemble woad under normal conditions, and, like the latter, yield a large amount of indigo on exposure to an atmosphere containing ammonia. G. T. M.

Formation of Indigo from *Indigoferæ* and from *Marsdenia tinctoria*. By PIETER VAN ROMBURGH (*Proc. k. Akad. Wetensch. Amsterdam*, 1899, 2, 344—348).—The aqueous extract of the leaves of *Marsdenia tinctoria* and certain of the *Indigoferæ* contains a soluble substance yielding indigotin on oxidation; indigo leaves retain the

power of decomposing indican even after extraction with ether, alcohol, acetone, or chloroform; the soluble compound which is thus liberated differs from indigo-white in being soluble in acids, and from indoxyl in its reactions with mineral acids or alkaline carbonates. G. T. M.

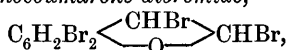
Fusion of Indigotin with Potassium Hydroxide. By W. HENTSCHEL (*J. pr. Chem.*, [ii], 1899, 60, 577—581. Compare Heumann and Bachofen, *Abstr.*, 1893, i, 270; Fritsche and Liebig, *Annalen*, 1841, 39, 76; Cahours, *Ann. Chim. Phys.*, 1845, [iii], 13, 113).—Indigo-blue dissolves but slowly in hot concentrated potassium hydroxide; at 150°, the products are indoxyl and chrysanic acid, $C_{16}H_{12}O_4N_2$, obtained respectively by reduction and oxidation of the indigotin. At 200—300°, the chrysanic acid becomes converted into anthranilic acid, but the indoxyl remains unaltered even at temperatures at which the anthranilic acid itself begins to decompose. The only bye-products are hydrogen and carbon dioxide. The action with sodium hydroxide is more violent; at 200°, the chief product is chrysanic acid, together with a little indoxyl; at 250°, practically pure anthranilic acid is obtained. J. J. S.

Salts of Indigotintrisulphonic Acid. By MAX HÖNIG (*Chem. Centr.*, 1899, ii, 1052; from *Festschr. Techn. Hochschule Brünn*, October, 1899).—The salts of indigotin-monosulphonic and -disulphonic acids are slightly soluble in water and are difficult to obtain in a crystalline form. Majmion prepared sodium indigotindisulphonate in the form of small needles arranged in tufts, but all the other salts were amorphous. *Indigotintrisulphonic acid* is formed by heating indigo with fuming sulphuric acid at 40—50°. The alkali salts are prepared by neutralising the aqueous solution of the acid, salting out with the corresponding alkali chloride, and crystallising from hot dilute alcohol. The sodium salt, $C_{16}H_7O_2N_2(SO_3Na)_3$, crystallises in copper-red, monoclinic needles which have a metallic lustre; it is easily soluble in hot 65 per cent. alcohol or in cold water, forming a solution which appears bluish-violet in reflected, and purple-red in transmitted, light. The potassium salt forms glittering, dark bluish-violet, rhombic leaflets and is rather soluble in water. The ammonium salt forms dark blue masses of very small crystals, and is very readily soluble in water or alcohol. The barium salt separates as a pale blue, crystalline precipitate somewhat soluble in water, but insoluble in barium chloride solution. The lead salt is a pale blue, amorphous precipitate and is rather soluble in water. The sodium or potassium salt can be titrated with centinormal potassium permanganate solution and might therefore be of use in the Neubauer-Löwenthal method of determining tannin, or in the Marx-Trommsdorff method of estimating nitric acid. E. W. W.

Tribromocoumarin and its Derivatives. By HUGO SIMONIS and G. WENZEL (*Ber.*, 1900, 33, 421—425).—Coumarin, when heated at 170° in a sealed tube with bromine, water, and some iodine, yields *tribromocoumarin*, $C_9H_2Br_3$ $\begin{matrix} & CH: CBr \\ & | \\ C_6H_2Br_2 & -O-CO \end{matrix}$, which forms long needles melting at 196°; on hydrolysing this with alcoholic potash, *dibromo-*

coumarilic acid, $\text{C}_6\text{H}_2\text{Br}_2\text{C}(\text{CH}=\text{O})\text{CO}_2\text{H}$, is obtained which crystallises in long needles melting at 276° ; the *potassium* and *sodium* salts crystallise with $2\text{H}_2\text{O}$, the *barium* and *copper* salts with $4\text{H}_2\text{O}$; the *methyl* ester separates from methyl alcohol in white needles melting at 151° , and boils above 360° without decomposition.

Dibromocoumarone, obtained by heating dibromocoumarilic acid, crystallises in colourless needles melting at 57.5° , and on treatment with bromine yields *dibromocoumarone dibromide*,



which forms colourless, prismatic crystals melting at 108° . Tribromocoumarin, on treatment with ammonia, yields the *amide* of dibromo- α -aminocoumaric acid, $\text{OH}\cdot\text{C}_6\text{H}_2\text{Br}_2\cdot\text{CH}\cdot\text{C}(\text{NH}_2)\cdot\text{CO}\cdot\text{NH}_2$, which forms prismatic crystals melting at 184° , and on hydrolysis yields an acid easily soluble in water.

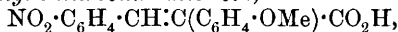
R. H. P.

Constitution of Naphthoylbenzoic Acid, Naphthanthraquinone, and Naphthanthracene. By SIEGMUND GABRIEL and JAMES COLMAN (*Ber.*, 1900, **33**, 446—469. Compare Abstr., 1898, i, 481 and 482).— α -Naphthoyl-*o*-benzoic acid is conveniently prepared by adding aluminium chloride to a hot solution of phthalic anhydride and naphthalene in carbon disulphide; its constitution is indicated from the results of fusion with potash, α -naphthoic acid being one of the products of hydrolysis. Naphthanthraquinone is shown to be an $\alpha\beta$ -compound by fusing it with potash, β -naphthoic and benzoic acids being thereby produced; it follows that naphthanthracene must also be an $\alpha\beta$ -derivative.

G. T. M.

Syntheses in the Phenanthrene Series: Synthesis of 1- and 3-Methoxyphenanthrene. By ROBERT PSCHORR, O. WOLFES, and W. BUCKOW (*Ber.*, 1900, **33**, 162—176).—Saligenin methyl ether (*o*-methoxybenzyl alcohol) is best prepared by leaving saligenin in contact with methyl iodide, methyl alcohol, and potassium hydroxide for 3 days at the ordinary temperature (compare Cannizzaro and Körner, *Ber.*, 1872, **5**, 436); at a higher temperature, *o*-methoxybenzyl methyl ether, $\text{OMe}\cdot\text{C}_6\text{H}_4\cdot\text{CH}_2\cdot\text{OMe}$, boiling at 229 — 230° , is obtained. *o*-Methoxybenzyl chloride forms six-sided plates, melts at 29 — 30° , and boils at 110 — 112° under 11 mm. pressure; it decomposes with loss of hydrogen chloride on keeping, forming a rose-coloured, brittle, vitreous mass. *o*-Methoxyphenylacetoneitrile, prepared by heating the chloride with dilute alcoholic potassium cyanide, crystallises from benzene on adding light petroleum in long, thin prisms, melts at 68° , boils at 141 — 143° under 15 mm. pressure, and has a peculiar, suffocating odour. There is also formed simultaneously a considerable quantity of *o*-methoxybenzylethyl ether, which, however, is best prepared by heating *o*-methoxybenzyl chloride with alcoholic sodium ethoxide; it is a colourless, strongly-refracting liquid, which boils at 230 — 232° under 754 mm. pressure. *o*-Methoxyphenylacetic acid, $\text{OMe}\cdot\text{C}_6\text{H}_4\cdot\text{CH}_2\cdot\text{CO}_2\text{H}$, obtained by hydrolysing the nitrile, crystallises from water in colourless, flattened prisms and melts at 124° .

α-o-Methoxyphenyl-o-nitrocinnamic acid,



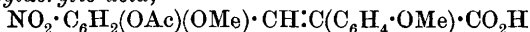
prepared by Perkin's reaction from *o*-methoxyphenylacetic acid and *o*-nitrobenzaldehyde, crystallises from alcohol in yellowish plates, melts at 219—220° (corr.), and on reduction with ferrous hydroxide yields the corresponding *amino-acid*; this crystallises from alcohol in yellowish prisms and melts at 169° (corr.). On decomposing its diazo-sulphate with copper powder, water and nitrogen are eliminated (compare Pschorr, Abstr., 1896, i, 303), and 1-methoxyphenanthrene-10-carboxylic acid obtained; the latter crystallises from alcohol in lustrous, slightly yellow leaflets, melts at 215° (corr.), and yields crystalline *barium*, *silver*, *lead*, *copper*, *platinum*, and *iron* salts. When distilled under 150—200 mm. pressure, carbon dioxide is evolved and 1-methoxyphenanthrene formed; this crystallises from alcohol in long, silky needles, sinters at 103°, and melts at 105—106°; the *picrate*, $\text{C}_{21}\text{H}_{15}\text{O}_8\text{N}_3$, crystallises from alcohol in tufts of yellowish-red needles and melts at 153° (corr.). Attempts to oxidise 1-methoxyphenanthrene and its carboxylic acid to the corresponding phenanthraquinones gave rise only to yellow, intractable, amorphous products.

Methyl p-methoxyphenylacetate, $\text{OMe} \cdot \text{C}_6\text{H}_4 \cdot \text{CH}_2 \cdot \text{CO}_2\text{Me}$, prepared by heating *p*-hydroxyphenylacetic acid with methyl iodide (2 mols.), potassium hydroxide, and methyl alcohol, boils at 263—265° under 760 mm., and at 155—157° under 23 mm. pressure.

α-p-Methoxyphenyl-o-nitrocinnamic acid crystallises from toluene in short golden prisms, from alcohol in lustrous plates, and melts at 177° (corr.); on reduction, it yields the *amino-acid*, $\text{C}_{16}\text{H}_{15}\text{O}_3\text{N}$, which crystallises from alcohol in long, yellow prisms mixed with colourless granules. Both modifications melt at the same temperature and have the same composition, moreover the colourless granules on heating are apparently converted into the yellow variety, and it is worthy of note that *α-phenyl-o-aminocinnamic acid* exists in two similar modifications (Pschorr, *loc. cit.*). 3-Methoxyphenanthrene-10-carboxylic acid, prepared in the same way as 1-methoxyphenanthrene-10-carboxylic acid, crystallises from alcohol in nearly colourless, lustrous needles, melts at 239°, and on being fused for a short time, and subsequently distilled in a vacuum, is partially decomposed into 3-methoxyphenanthrene. This crystallises from dilute alcohol in lustrous plates, melts at 63° and yields a *picrate*, which forms red needles melting at 124.5° (corr.). 3-Methoxyphenanthraquinone, prepared by oxidising 3-methoxyphenanthrenecarboxylic acid with chromic acid in acetic acid solution, crystallises from alcohol in orange needles and melts at 208° (corr.).

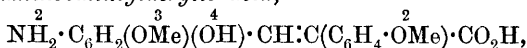
W. A. D.

Syntheses in the Phenanthrene Series; ψ -Thebaol. By ROBERT PSCHORR (*Ber.*, 1900, 33, 176—183).—*α-o-Methoxyphenyl-β-o-nitroacetylvanillylacrylic acid*,



[CH : NO₂ : OMe : OAc = 1 : 2 : 3 : 4], prepared by Perkin's reaction from *o*-methoxyphenylacetic acid (preceding abstract) and nitroacetylvanillin [CHO : NO₂ : OMe : OAc = 1 : 2 : 3 : 4], crystallises from toluene in feebly yellow prisms, sinters at 210°, melts at 217—218° (corr.), and

on reduction with ammoniacal ferrous hydroxide yields *α*-*o*-methoxyphenyl-β-*o*-aminovanillylacrylic acid,

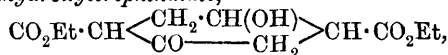


which sinters at 60°, melts at about 90°, and cannot be recrystallised as it is easily decomposed; in toluene solution, the composition gives rise to 2 : 7-*dihydroxy*-8-*methoxy*-3-*o*-methoxyphenylquinoline, which separates in nearly colourless prisms and melts at 255—256° (corr.). *α*-ψ-*Thebaolcarboxylic acid* (6-*hydroxy*-1 : 5-*dimethoxyphenanthrene*-10-*carboxylic acid*), prepared from the foregoing amino-acid by the method adopted for 1-methoxyphenanthrene-10-*carboxylic acid* (preceding abstract), crystallises from dilute alcohol or acetic acid in nearly colourless, six-sided plates, and melts at 231° (corr.); the *acetyl* derivative, $\text{OAc} \cdot \text{C}_{14}\text{H}_6(\text{OMe})_2 \cdot \text{CO}_2\text{H}$, prepared by acting on the potassium salt of the acid with acetic anhydride, crystallises from the same solvents in flat prisms and melts at 220—227° (corr.); if, however, the hydroxy-acid is warmed with acetic anhydride containing a small quantity of concentrated sulphuric acid, the *anhydride*, $\text{C}_{38}\text{H}_{30}\text{O}_{11}$, of the acetyl derivative is obtained, which crystallises from glacial acetic acid in irregular leaflets and melts at 236—238°.

α-ψ-*Thebaol* (6-*hydroxy*-1 : 5-*dimethoxyphenanthrene*), prepared by heating its carboxylic acid with acetic acid for 5 hours at 215—225°, crystallises from dilute alcohol or glacial acetic acid in reddish-brown, irregular leaflets, melts at 164—165° (corr.), and yields a *sodium* salt crystallising in lustrous leaflets; the *acetyl* derivative, $\text{C}_{18}\text{H}_{16}\text{O}_4$, forms colourless, radiating prisms, melts at 96—97°, and, when heated with acetic anhydride containing a little concentrated sulphuric acid, yields a blackish-blue, crystalline powder, which contains sulphur and resembles indigo in appearance. 1 : 5 : 6-*Trimethoxyphenanthrene*, prepared by heating ψ-thebaol with methyl iodide and potassium hydroxide, crystallises from alcohol in colourless leaflets and melts at 135° (corr.); the *picrate*, $\text{C}_{23}\text{H}_{19}\text{O}_{10}\text{N}_3$, forms dark-red, lustrous needles and melts at 126° (corr.), whilst the *dibromo*-derivative, $\text{C}_{14}\text{H}_5\text{Br}_2(\text{OMe})_3$, crystallises from glacial acetic acid in nearly colourless needles melting at 139—141° (corr.).

Since both 1 : 5-*dimethoxy*-6-*acetoxyphenanthrene* and its 10-*carboxylic acid* resemble 1-methoxyphenanthrene (preceding abstract) in not yielding the corresponding phenanthraquinones on oxidation, and differ in this respect from 3-methoxyphenanthrenecarboxylic acid (preceding abstract) and acetylthebaol (Freund, Abstr., 1897, i, 495), it appears probable that thebaol does not contain a methoxyl group in position 1, but is either 4 : 5- or 4 : 7-*dimethoxy*-6-*hydroxyphenanthrene* (compare Freund, *loc. cit.*).
W. A. D.

Hydrogenisation of Ethyl Succinylsuccinate. By ROBERT STOLLÉ (*Ber.*, 1900, 33, 390—392).—*Ethyl dihydrosuccinylsuccinate* or *tetrahydrodihydroxyterephthalate*,



or $\text{CO}_2\text{Et} \cdot \text{C} \begin{array}{c} \text{CH}_2 \cdot \text{CH}(\text{OH}) \\ \text{C}(\text{OH}) \text{---} \text{CH}_2 \end{array} \text{CH} \cdot \text{CO}_2\text{Et}$, a viscous oil which boils

at 218—220° under 14 mm. pressure, dissolves sparingly in water, and reduces alkaline permanganate; the alcoholic solution is indifferent towards ferric chloride. The *methyl* ester boils at 211—212° under 14 mm. pressure.

Ethyl tetrahydrosuccinylsuccinate (*hexahydrodihydroxyterephthalate*, $\text{CO}_2\text{Et} \cdot \text{CH} \begin{smallmatrix} \text{CH}_2 \cdot \text{CH}(\text{OH}) \\ \text{CH}(\text{OH}) \cdot \text{CH}_2 \end{smallmatrix} \text{CH} \cdot \text{CO}_2\text{Et}$, crystallises from alcohol, and melts at 135—136°; it is somewhat soluble in water, and is indifferent towards alkaline permanganate. The *methyl* ester melts at 187°.

Ethyl hydrogen dihydroterephthalate, $\text{CO}_2\text{Et} \cdot \text{C} \begin{smallmatrix} \text{CH}_2 \cdot \text{CH} \\ \text{CH} \cdot \text{CH}_2 \end{smallmatrix} \text{C} \cdot \text{CO}_2\text{H}$, crystallises from alcohol in slender needles, and melts at 178—179°.
M. O. F.

Usnic Acid. By OSKAR WIDMAN (*Annalen*, 1899, 310, 230—264).—Usnic acid has been isolated from a large number of lichens, and the descriptions of various specimens differ somewhat widely among themselves. This is explained by the fact, discovered by the author, that usnic acid occurs in two modifications, which are optical antipodes; these melt at 203°, and the inactive mixture melts at 192°. So far as can be ascertained from existing data, the character of the usnic acid produced by a lichen is not influenced by position, latitude, height above sea-level, or season of year.

d-Usnic acid, $\text{C}_{18}\text{H}_{16}\text{O}_7$, found in several varieties of *Usnea barbata*, melts at 203°; specimens prepared from *U. barbata hirta*, *U. barbata γ-plicata*, and *Cladonia rangiferina silvatica*, gave $[\alpha]_D +49.2^\circ$, 49.3° , and 49.55° respectively. *l*-Usnic acid also melts at 203°, and gave $[\alpha]_D -49.58^\circ$ and -48.55° , according as the source was *Cetraria nivalis* or *Cladonia rangiferina alpestris*. *i*-Usnic acid crystallises from benzene and acetic acid in yellow needles, long, four-sided prisms, or six-sided plates, and melts at 191—192°. The *sodium* salts contain $2\text{H}_2\text{O}$, which is easily removed in the case of the active compound.

The *d*- and *l*-oximes of usnic acid melt and slowly decompose at 100—145°. The *anhydride*, $\text{C}_{18}\text{H}_{15}\text{O}_6\text{N}$, prepared by heating *d*-usnic acid in benzene with hydroxylamine acetate, crystallises from ethyl acetate in long, lustrous prisms or four-sided plates, and melts at 230° without evolving gas; sodium methoxide converts it into the compound, $\text{C}_{19}\text{H}_{19}\text{O}_7\text{N}$, which crystallises in quadratic prisms and melts at 147°. The *inactive oxime* crystallises in prismatic needles, and melts and decomposes at 243—244°; the *acetyl* derivative forms pale yellow leaflets and melts at 194°, when it evolves gas.

The *d*- and *l*-semicarbazones of usnic acid decompose suddenly at 219—220°, and the *inactive* modification decomposes at 211°.

The *d*-*anilide* separates from a mixture of benzene and petroleum in four-sided pyramids, and usually melts at 138°, but the melting point is sometimes as high as 152—153°, or even 157—158°, if the substance is previously dried at 110°. It has $[\alpha]_D +28.6^\circ$ in chloroform, and the *l*-*anilide*, which resembles it, has $[\alpha]_D -28.45^\circ$. The *inactive anilide* crystallises from glacial acetic acid in cubes, and melts at

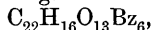
232°. The *d*-oximeanilide, $C_{24}H_{22}O_5N_2$, prepared from the *d*-anilide by the action of hydroxylamine, dissolves in potassium hydroxide, and melts at 222—230°.

The *inactive amide*, $C_{18}H_{17}O_6N$, obtained by heating *i*-usnic acid with alcoholic ammonia in a reflux apparatus, crystallises from glacial acetic acid in rhombic plates, and melts at 245—246°. The *piperidine* salt of *i*-usnic acid crystallises in leaflets, and gradually dissolves at 140°.

The *bisphenylhydrazide anhydride* of *d*-usnic acid, $C_{30}H_{26}O_4N_4$, crystallises from glacial acetic acid and melts at 233°, and is identical with the phenylhydrazine derivative of “*α*-usnic acid” described by Hesse. The *bisphenylhydrazide anhydride* of *i*-usnic acid melts at 267°. The *m-p-toluylenediamide* of *i*-usnic acid separates from glacial acetic acid in somewhat indefinite crystals, and melts at 217°, when it blackens and evolves gas.

M. O. F.

Derivatives of Carminic Acid. By CARL LIEBERMANN, P. HÖRING, and FRITZ WIEDERMANN [and in part MESSINGER and I. FRÄNCKEL] (*Ber.*, 1900, **33**, 149—159. Compare Abstr., 1898, i, 682).—Carminic acid forms an *acid silver* salt, $C_{22}H_{21}O_{13}Ag$, obtained as an orange-coloured precipitate on the addition of silver nitrate to an alcoholic solution of the acid. The *ethylamine* salt, $C_{22}H_{22}O_{13}(NH_2Et)_3$, and the *benzylamine* salt, $C_{22}H_{22}O_{13}(NH_2 \cdot C_6H_5)_3$, both form small, brown needles and dissociate on heating. *Hexabenzoylcarminic acid*,



is obtained by the action of benzoyl chloride on carminic acid, and forms an orange-red powder which is only slowly dissolved by alkalis.

The first product of the action of bromine on carminic acid dissolved in acetic acid is *dibromocarminic acid hydrobromide*, $C_{22}H_{20}O_{13}Br_2 \cdot HBr$; it forms small, lemon-yellow crystals which easily evolve hydrogen bromide and carbon dioxide, and give *decarboxydibromocarminic acid*, $C_{21}H_{20}O_{11}Br_2$. This is obtained in the form of small, hygroscopic needles and has colouring properties similar to those of cochineal; its formation affords a proof of the presence of a carboxyl group in carminic acid, which, however, cannot owe its colouring properties to this group. The *hexa-acetyl* derivative is an orange-red powder, and the *hexabenzoyl* derivative is precipitated from benzene by light petroleum as an orange-red powder which melts at 160—170° and is insoluble in alkalis.

The authors have repeated the experiments of Will and Leymann (Abstr., 1886, 252) on *α*- and *β*-bromocarmin. *β*-Bromocarmin forms well-characterised salts with aromatic bases; the *p-toluidine* salt is precipitated in the form of red needles on mixing a solution of *β*-bromocarmin with the base, and serves to separate it from *α*-bromocarmin, which only forms a similar salt with difficulty. R. H. P.

Allotropy of Benzophenone. By WILLIAM OECHSNER DE CONINCK (*Compt. rend.*, 1900, **130**, 40—42).—When benzophenone is dissolved in dilute alcohol and a current of air passed through the solution for many weeks, the liquid being protected from light, the benzophenone is converted into the unstable modification melting at

27°. No similar change is produced by exposing the crystallised substance to light. Rapid dissolution of the benzophenone in dilute alcohol facilitates the conversion into the allotropic modification. It is noteworthy that in these experiments the benzophenone is not oxidised.

C. H. B.

Dibenzylideneacetoneoxime. By GAETANO MINUNNI (*Gazzetta*, 1899, 29, ii, 387—404. Compare Abstr., 1898, i, 194).—The compound, melting at 142—144°, obtained by the action of hydroxylamine hydrochloride on dibenzylideneacetone, and described (*loc. cit.*) as a dihydroisoxazole derivative, proves to be *dibenzylideneacetoneoxime*, $C(CH:CHPh)_2:N\cdot OH$; it forms an *acetyl* and a *benzoyl* derivative, which crystallise from alcohol in beautiful, silky, white needles, the former melting at 93—94° and the latter at 111·5—112°.

Dibenzylideneacetonephenylhydrazone, $C_{23}H_{20}N_2$, obtained by the action of phenylhydrazine on either the acetone or its oxime, separates from alcohol in tufts of yellow needles melting at 146·5—147·5°.

The action of concentrated sulphuric acid on dibenzylideneacetoneoxime gives rise to an isomeric *substance* which crystallises from alcohol in beautiful, white, nacreous leaflets melting at 110—111°; it is insoluble in alkalis or dilute mineral acids.

In the dibenzylideneacetoneoxime mother liquors, two other compounds are found: one, $C_{17}H_{18}O_2N_2$, melting at 200—202° (*loc. cit.*), and the other having the same composition and separating from its ethereal solution by the addition of light petroleum in the form of star-shaped crystals melting at 163—164°.

T. H. P.

Action of Hydroxylamine Hydrochloride on Ketones of the Type $CO(CH:CHR)_2$ in presence of Sodium Acetate. By GAETANO MINUNNI and C. CARTA-SATTA (*Gazzetta*, 1899, 29, ii, 404—420).—The compound, $C_{17}H_{18}O_2N_2$, melting at 200—202°, obtained from the dibenzylideneacetoneoxime mother liquors (see preceding abstract), is shown to be *α-dibenzylideneacetonehydroxylamineoxime*, having the constitution $OH\cdot NH\cdot CHPh\cdot CH_2\cdot C(N\cdot OH)\cdot CH:CHPh$ or $CH_2Ph\cdot CH(NH\cdot OH)\cdot C(N\cdot OH)\cdot CH:CHPh$; the *dibenzoyl* derivative, $C_{31}H_{26}O_4N_2$, separates from alcohol in acicular crystals melting at 147—148°, which become slightly red on exposure to the air. The *diacetyl* compound, $C_{21}H_{22}O_4N_2$, crystallises from alcohol in white, acicular needles melting at 156—157°. By the action of hydrochloric acid on the *α*-oxime, hydroxylamine, dibenzylideneacetone, and benzaldehyde are formed, together with the *β*-modification melting at 164°, which is also found in the benzylideneacetoneoxime mother liquors (*loc. cit.*).

Dipiperonalacetone reacts with hydroxylamine hydrochloride in presence of sodium acetate in a manner similar to dibenzylideneacetone, a compound, $C_{19}H_{18}O_6N_2$, being obtained; it separates from alcohol in pale yellow, mammillary masses melting at 177—179°.

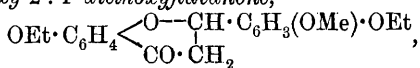
T. H. P.

3:3'-Dihydroxyflavone. By B. VON HARPE and STANISLAUS VON KOSTANECKI (*Ber.*, 1900, 33, 322—325).—2'-Hydroxy-3:4'-diethoxychalkone, $OEt\cdot C_6H_3(OH)\cdot CO\cdot CH:CH\cdot C_6H_3\cdot OEt$, obtained by the condensation of *m*-ethoxybenzaldehyde and 2-hydroxy-4-ethoxyacetophenone

under the conditions described previously (Abstr., 1898, i, 369), crystallises from alcohol in yellow plates melting at 85° , dissolves in concentrated sulphuric acid to a deep yellow solution, yields a sparingly soluble *sodium* salt, and an *acetyl* derivative melting at 68° . The *acetyl dibromide*, $\text{OEt} \cdot \text{C}_6\text{H}_3(\text{OAc}) \cdot \text{CO} \cdot \text{CHBr} \cdot \text{CHBr} \cdot \text{C}_6\text{H}_4 \cdot \text{OEt}$, crystallises from alcohol in colourless needles melting at 105° , and, when warmed in alcoholic solution with concentrated potassium hydroxide, is converted

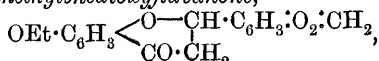
into 3 : 3'-*diethoxyflavone*, $\text{OEt} \cdot \text{C}_6\text{H}_3 \begin{smallmatrix} \text{O} - \text{C}_6\text{H}_4 \cdot \text{OEt} \\ \text{CO} \cdot \text{CH} \end{smallmatrix}$. This crystallises from dilute alcohol in colourless needles melting at 153 — 154° and is soluble in concentrated sulphuric acid to a pale yellow solution with a bluish-green fluorescence; when hydrolysed with sodium ethoxide, it is quantitatively converted into *m*-ethoxybenzoic acid and 2-hydroxy-4-ethoxyacetophenone, and when boiled for two hours with hydriodic acid of sp. gr. 1.96, it yields 3'-*hydroxy-3-ethoxyflavone*, which crystallises in colourless plates, melts at 263 — 264° , dissolves in sulphuric acid to a blue solution, forms a sparingly soluble *sodium* salt, and gives an *acetyl* derivative melting at 126 — 127° . The prolonged action of hydriodic acid converts the diethyl ether into 3 : 3'-*dihydroxyflavone*; this is readily soluble in alcohol, crystallises in glistening, monohydrated needles, and in the anhydrous form melts at 277 — 278° ; its *diacetyl* derivative melts at 152 — 153° . J. J. S.

2 : 3' : 4'-*Trihydroxyflavone*. By STANISLAUS VON KOSTANECKI and TH. SCHMIDT (*Ber.*, 1900, 33, 326—330. Compare Abstr., 1899, i, 370).—3'-*Methoxy-2 : 4'-diethoxyflavanone*,



is obtained by the condensation of 3-methoxy-4-ethoxybenzaldehyde (ethylvanillin) with 2-hydroxy-5-ethoxyacetophenone in the presence of alcohol and concentrated sodium hydroxide solution; a red bye-product is formed at the same time, and can only be removed by repeated crystallisation from alcohol. It crystallises in colourless needles, melts at 127 — 128° , dissolves in concentrated sulphuric acid or in alcoholic potash to red solutions, and in alcohol to a pale green, fluorescent solution. By the action of bromine in carbon disulphide solution, it is converted into a *monobromo*-derivative, $\text{OEt} \cdot \text{C}_6\text{H}_3 \begin{smallmatrix} \text{O} \\ \text{CO} \end{smallmatrix} \text{C}_2\text{H}_2\text{Br} \cdot \text{C}_6\text{H}_3(\text{OMe}) \cdot \text{OEt}$, which crystallises in colourless needles melting and decomposing at 133° ; strong alkali converts the bromine derivative into 3'-*methoxy-2 : 4'-diethoxyflavone*, $\text{OEt} \cdot \text{C}_6\text{H}_3 \begin{smallmatrix} \text{O} - \text{C}_6\text{H}_3(\text{OMe}) \cdot \text{OEt} \\ \text{CO} \cdot \text{CH} \end{smallmatrix}$, which forms colourless needles melting at 168° , and soluble in alcohol to a blue, fluorescent solution.

2-*Ethoxy-3 : 4'-methylenedioxyflavanone*,



obtained from piperonal and 2-hydroxy-5-ethoxyacetophenone, crystallises in colourless needles melting at 144° ; its crude *monobromo*-derivative, when treated with alkali, yields 2-*ethoxy-3' : 4'-methylenedioxyflavone*,

melting at 204°. When heated with sodium ethoxide, these flavones are hydrolysed in exactly the same manner as other flavone derivatives (compare preceding abstract).

2 : 3' : 4'-*Trihydroxyflavone*, obtained when either of the above flavone derivatives is heated with concentrated hydriodic acid, forms yellowish, crystalline crusts melting and decomposing at 328°, dissolves readily in sodium hydroxide, and gives a yellow dye with alumina mordants; its *diacetyl* derivative melts at 208—209°. J. J. S.

Formation of Flavone from its Decomposition Products. By STANISLAUS VON KOSTANECKI and JOSEF TAMBOR [with J. BONGARTZ] (*Ber.*, 1900, **33**, 330—334).—The first product, obtained by the action of alkalis on flavone is *o*-hydroxybenzoylacetophenone, formed by the rupture of the γ -pyrone ring; this may then undergo acid hydrolysis into benzoic acid and *o*-hydroxyacetophenone, or ketonic hydrolysis into salicylic acid and acetophenone. The authors have succeeded in synthesising flavone from both of these pairs of compounds. When a mixture of ethyl *o*-ethoxybenzoate and acetophenone is treated with metallic sodium and the mixture left for 24 hours, or when a mixture of *o*-ethoxyacetophenone and ethyl benzoate is treated as recommended by Emilewicz, Kostanecki, and Tambor in the preparation of 2 : 4 : 6-trimethoxybenzoylacetophenone (*Abstr.*, 1899, i, 911), the product is *o*-ethoxybenzoylacetophenone, which, on treatment with concentrated hydriodic acid, yields flavone. J. J. S.

Action of Hydroxylamine and Phenylhydrazine on Dithiobenzoylacetone. By VICTOR VAILLANT (*Bull. Soc. Chim.*, 1900, [iii], **23**, 36—37).—Dithiobenzoylacetone, $S_2(CHAcBz)_2$ (*Abstr.*, 1899, i, 599), reacts with hydroxylamine and phenylhydrazine to form the corresponding *oxazoledisulphide*, $S_2(C_3ONMePh)_2$, and *pyrazoledisulphide*, $S_2(C_3N_2MePh)_2$, respectively. The former crystallises from boiling alcohol in nacreous, yellow scales melting at 91—92°, whilst the latter is a crystalline, yellow powder melting at 162°. N. L.

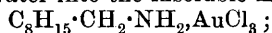
Conversion of Dihydrocarvone into Carvenone by means of Formic Acid. By AUGUST KLAGES (*J. pr. Chem.*, 1899, [ii], **60**, 544).—A reply to Kondakoff on a question of priority (this vol., i, 104).

E. G.

Amines containing the Camphor Nucleus. By G. BLANC (*Compt. rend.*, 1900, **130**, 38—40).—*Dihydroisolaureonamine*,



obtained quantitatively by the reduction of isolaureonolnitrile by sodium in presence of alcohol, is a mobile, colourless liquid boiling at 185° and of sp. gr. 0.8619 at 15°. It absorbs carbon dioxide from the air, gives the carbylamine reaction, and combines energetically with methyl iodide. The *hydrochloride* forms nacreous lamellæ which melt at about 265°; the *platinichloride*, a yellow, crystalline powder; the *aurichloride*, bright yellow needles, which melt at 203—205°, and are converted by boiling water into the insoluble modification,



the *nitrate*, nacreous leaflets which melt at 179°; the *nitrite*, white needles stable in a hot neutral aqueous solution; the *sulphate*, white

plates melting at 249° ; the *oxalate*, slender needles melting at 243° ; the *picrate*, golden-yellow lamellæ melting at 215° . All these salts decompose at their melting points.

The *benzoyl* derivative, $C_8H_{15} \cdot CH_2 \cdot NHBz$, forms large, striated prisms melting at 51° ; the *carbamide*, $NH_2 \cdot CO \cdot NH \cdot CH_2 \cdot C_8H_{15}$, slender needles melting at 102° ; the *oxamide*, transparent tablets melting at $133-134^{\circ}$.

Dihydroisolaureonethylamine, $C_8H_{15} \cdot CH_2 \cdot NHEt$, is a colourless, mobile liquid boiling at 205° , and of sp. gr. 0.8417 at 15° . Its *nitroso*-derivative is an oily liquid; the *hydrochloride* forms nacreous plates; the *platinichloride*, orange-red needles; the *nitrite*, slender needles melting at 161° , stable in a hot neutral solution, but yielding the nitroso-derivative in presence of acids; the *sulphate* melts at $124-125^{\circ}$, and the *picrate* at $112-114^{\circ}$.

Dihydroisolaureonediethylamine boils at 235° ; its hydrochloride forms small prisms melting at $182-183^{\circ}$, and the *platinichloride* is gummy.

Homodihydroisolaureonamine, $C_8H_{15} \cdot CHMe \cdot NH_2$, obtained by reducing the oxime of acetylisolaureolene, boils at 190° , and has a sp. gr. 0.9558 at 15° ; its hydrochloride melts and decomposes at about 230° ; the *platinichloride* is a crystalline, orange-yellow powder. C. H. B.

Nature of Inactive Carvoxime. By H. W. BAKHUIS ROOZEBOOM (*Proc. K. Akad. Wetensch. Amsterdam*, 1899, 2, 160-162).—Investigation of the solidifying points of mixtures of *d*- and *l*-carvoxime leads to the conclusion that the one containing 50 per cent. of each and melting about 20° higher than either active modification, is not a racemic compound, but a pseudo-racemic mixed crystal. There is a fall of temperature between the beginning and the end of solidification, except for the mixture containing 50 per cent. of each; in no case, however, can solidification be observed corresponding with a eutectic point as would be the case were inactive carvoxime a racemic compound. Mixed crystals seem to be formed on solidification at all concentrations—a view supported by analysis of the crystals deposited.

This is the first example of a series of mixed crystals with a maximum melting point. It was found, moreover, that down to 10° no change of these mixed crystals into a racemic compound took place. J. C. P.

Tanacetone and its Derivatives. By FRIEDRICH W. SEMMLER (*Ber.*, 1900, 33, 275-277).—The ketonic acid obtained on carefully oxidising isothujone with potassium permanganate (Wallach, *Abstr.*, 1897, i, 246) boils at 273° , and is thereby converted into the keto-lactone, $C_{10}H_{16}O_3$ (m. p. 43° ; oxime, m. p. 155°), which is formed on oxidising thujamenthone with chromic acid; on further oxidation, the keto-lactone yields β -isopropylævulinic acid, and hence probably has

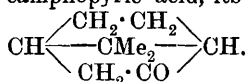
the structure $O \begin{array}{c} \diagup CMeAc \\ \diagdown CO \end{array} \begin{array}{c} CHPr^{\beta} \\ | \\ CH_2 \end{array}$, whilst the formulæ

$$CMe \begin{array}{c} \diagup CMe \cdot CHPr^{\beta} \\ \diagdown CO \end{array} \begin{array}{c} | \\ CH_2 \end{array}, CHMe \begin{array}{c} \diagup CHMe \cdot CHPr^{\beta} \\ \diagdown CO \end{array} \begin{array}{c} | \\ CH_2 \end{array},$$

and $\text{CH}_2 \begin{array}{c} \text{CPr}^s - \text{CH}_2 \\ | \\ \text{CH} \cdot \text{CHMe} \end{array} \text{CO}$ must be given to isothujone, thujamethone, and tanacetone respectively.

W. A. D.

Compounds of the Fenchone Series. By OTTO WALLACH [with EDGARD NEUMANN and WILHELM VON WESTPHALEN] (*Chem. Centr.*, 1899, ii, 1052—1053; from *Nachr. k. Ges. Wiss. Göttingen*, 1899, No. 2).—The *nitrile*, $\text{C}_9\text{H}_{13}\text{N}$, formed by warming the oxime of *D-d*-fenchocamphorone with dilute sulphuric acid (1 : 2), has the odours of camphonitrile and fenchonitrile and boils at 212—215°. The corresponding *acid*, $\text{C}_8\text{H}_{13} \cdot \text{CO}_2\text{H}$, forms a silver salt which is not affected by light. The *base*, $\text{C}_9\text{H}_{15} \cdot \text{NH}_2$, obtained by reducing the nitrite with alcohol and sodium, yields a carbamide, $\text{NH}_2 \cdot \text{CO} \cdot \text{NH} \cdot \text{C}_9\text{H}_{15}$, which melts at 131—132°. Since fenchocamphorone on oxidation with nitric acid forms camphopyric acid, its constitution is probably



The yellow compound, $\text{C}_{11}\text{H}_{16}\text{O}_2$, which melts at 96°, and is obtained by distilling lead fenchocarboxylate, forms a *dioxime*, $\text{C}_{11}\text{H}_{16}(\text{N} \cdot \text{OH})_2$, melting at 198—199° and soluble in water. The compound $\text{C}_{11}\text{H}_{16}\text{O}_2$ is probably therefore an *o*-diketone or an *o*-hydroxyketone capable of acting in the tautomeric diketonic form. The pinacene, $\text{C}_{20}\text{H}_{34}\text{O}_2$, which melts at 122°, is also formed in the preparation of fenchocarboxylic acid. Fencholenic acid exists in two modifications. Two fencholenamides are known; the one melts at 113—114°, and the other at 85—86°. The latter corresponds with Cockburn's fencholenic acid which melts at 70°.

E. W. W.

Oxidation of Pinene. By OTTO WALLACH and A. SCHÄFER (*Chem. Centr.*, 1899, ii, 1052; from *Nachr. k. Ges. Wiss. Göttingen*, 1899, No. 2).—The volatile compound which is formed together with α -pinonic acid when pinene is oxidised by von Baeyer's method, is found to be the ketone nopinone. Nopinone is formed by the further oxidation of the small quantity of nopinic acid which von Baeyer found was always produced by the oxidation of pinene. The formation of benzylidenenopinone is in accordance with von Baeyer's theory that in nopinone the CO group is contiguous to a CH_2 group.

E. W. W.

Genesis of Terpenes in Lavender. By EUGÈNE CHARABOT (*Compt. rend.*, 1900, 130, 257—259. Compare *Abstr.*, 1898, i, 595, and this vol., ii, 101).—An examination of three samples of essence of lavender taken from the plant at the budding, flowering, and fading stages shows that the specific gravity and optical activity of the essence increase and the amount of free acid present decreases as the plant attains maturity. The maximum quantity of esters is obtained from the plant when in flower and the amount present in the essence from the specimens with faded flowers is greater than that extracted from the young plant. The proportion of alcohol whether free or combined diminishes until the flowers have blossomed and at the same time the relative amount of esters increases; the essence from the mature

plant with faded flowers, however, contains more alcohol and less esters.

These results seem to indicate that during development the esters are produced by the direct action of the acids on the linalool and that during this period a portion of the alcohol is dehydrated; when the flowers begin to wither, esterification ceases; and then the proportion of total alcohol increases. The formation of esters and terpenes, which takes place in the green parts of the plant, is probably due to chlorophyllous evaporation. G. T. M.

Essence of Geranium. By JEANCARD and SATIE (*Bull. Soc. Chim.*, 1900, [iii], 23, 37—39).—Six specimens of essential oil of geranium obtained from Cannes, Spain, Corsica, Africa, Reunion, and India respectively were examined, with the following results. Sp. gr. at 15°, 0.8905—0.9073; rotation per 100 mm. at 15°, -0.48° to -9.40° ; acid number (mg. of KOH per 1 gram), 9.6—56.0; saponification number, 43.0—74.0; esters as $C_{12}H_{20}O_2$, 6.65—11.30 per cent.; alcohols as $C_{10}H_{18}O$, 61.31—84.62 per cent. All the samples contained free acid, the amount of which was increased by exposure to the air. The solubility of the oils in alcohol was nearly constant, 1 vol. being dissolved by 0.9—1.0 vol. of 80 per cent. alcohol, or 2—2.3 vols. of 70 per cent. alcohol, at 15°. N. L.

Composition of East Indian Essence of Sandalwood. By M. GUERBET (*Compt. rend.*, 1900, 130, 417—420).—A specimen of essence of sandalwood from Bombay was of a pale yellow colour and oily consistence, and had a sp. gr. 0.9684 at 0° and a rotatory power $[\alpha]_D -21.1^{\circ}$. It contained 90.1 per cent. of alcohols calculated as $C_{15}H_{26}O$, and esters corresponding with 7 mg. of potassium hydroxide per 1 gram of the oil; no free acid or base was detected. The following compounds were isolated from the essence: (1) Two isomeric sesquiterpenes: *a-santalene*, boiling at 252—252.5° and having a sp. gr. 0.9134 at 0° and a rotatory power $[\alpha]_D -13.98^{\circ}$, and *β-santalene* boiling at 261—262° and having a sp. gr. 0.9139 at 0° and a rotatory power $[\alpha]_D -28.55^{\circ}$; both are colourless, oily liquids of feeble odour. *β-Santalene* has previously been isolated by Soden and Müller (*Pharm. Zeit.*, 44, 258). (2) A mixture of alcohols, $C_{15}H_{26}O$, distilling at 183—197° under 37 mm. pressure and having rotatory powers ranging from $[\alpha]_D -9.4^{\circ}$ to $[\alpha]_D -25.3^{\circ}$; this probably consists of *a-* and *β-santalols*, corresponding with *a-* and *β-santalene*. (3) An aldehyde, *santalal*, $C_{15}H_{24}O$, a colourless, oily liquid of strong pepper-like odour and boiling at 180° under 40 mm. pressure; it forms a *semicarbazone* which crystallises in small needles melting at 212°. (4) *Santalalic acid*, $C_{15}H_{24}O_2$, a colourless, viscous liquid which boils at 210—212° under 20 mm. pressure and is insoluble in water; the *potassium*, *sodium*, and *barium* salts are crystalline compounds which are decomposed by carbon dioxide. This acid is also formed when *santalal* is oxidised with chromic acid in acetic acid solution. (5) *Teresantalic acid*, $C_{10}H_{14}O_2$, crystallises from alcohol in large, colourless prisms melting at 157° and boiling at 183° under 28 mm. pressure. The *potassium* salt was obtained as a nacreous, crystalline mass; the *calcium* salt crystallises with $2H_2O$. (6) 0.2—0.3 per cent. of odorous substances,

which could not be obtained in the pure state; small quantities of acetic and formic acids were also found. N. L.

Curangin, the Glucoside of *Curanga amara*. By S. E. BOORSMA (*Chem. Centr.*, 1899, ii, 991—992, 1125; from *Ned. Tijds. Pharm.*, 11, 303—316, 327—336. Compare *Mededeel. uits'-Land-Plantentuin*, 18).—The bitter febrifuge curangin, $C_{48}H_{77}O_{20}$, may be extracted from the *Scrophulariaceæ* by means of ethyl acetate. This glucoside is easily soluble in ethyl or methyl alcohol, or in acetone or ethyl acetate containing water; 100 parts of water dissolve 0.18 part. The solutions are neutral. When heated at 100° , curangin loses 7—10 per cent. of water, but the residue regains this amount on exposure to air. Its colour reactions, &c., are described in detail. By the action of benzoyl chloride and sodium hydroxide solution, it forms a compound, $C_{48}H_{69}O_{20}Bz_3$, which melts at 128° , and with phenylhydrazine it yields a compound which contains nitrogen and melts at 163° . Attempts to prepare a bromide failed, as the hydrogen bromide which is formed decomposes the glucoside. When curangin is boiled with a 2 per cent. solution of hydrogen chloride in alcohol, it is decomposed into *curangaegenin* and a sugar, which appears to consist mainly of rhamnose. The crude curangaegenin contains two compounds, of which the one (A) present in the larger quantity, is soluble in ether, and is apparently partially converted into the other (B) by prolonged boiling with the alcoholic acid solution; (B) is insoluble in ether. Both substances are easily soluble in ethyl acetate, acetone, glacial acetic acid, or methyl, ethyl, or amyl alcohol. Their colour reactions are given in detail. E. W. W.

Arrow Poison of Wakamba (German East Africa). By LUDWIG BRIEGER (*Chem. Centr.*, 1899, ii, 1130; from *Deutsch. med. Woch.*, 25, No. 39).—The Wakamba arrow poison is a glucoside, $C_{29}H_{46}O_{19}$, and somewhat resembles Arnaud's ouabain (*Abstr.*, 1888, 848). It crystallises from a hot saturated solution in anhydrous needles which melt at 182 — 184° , but the plates obtained by allowing the compound to crystallise more slowly contain 20 per cent. of water and melt at 93 — 94° . It is insoluble in ether, ethyl acetate, chloroform, or benzene, slightly soluble in cold water, and more easily soluble in hot water or alcohol. The specific rotatory power for a 4 per cent. aqueous solution is $[\alpha]_D - 37^{\circ}$. When the compound is boiled with dilute hydrochloric or sulphuric acid, a yellow, amorphous precipitate is formed; this is easily soluble in alcohol, and is not poisonous. The filtrate reduces Fehling's solution, although the poison itself is incapable of doing so. The filtrate may also be fermented, and yields an amorphous glucosazone. The aqueous solution of the glucoside does not give precipitates with the ordinary alkaloidal reagents. A dose of 0.3 mg. per kilogram of body weight proved fatal in the case of dogs in 2 hours.

An amorphous, non-poisonous substance was also isolated.

E. W. W.

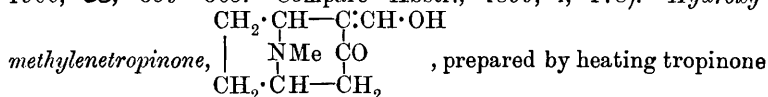
Chlorophyll. By LEO MARCHLEWSKI (*J. pr. Chem.*, 1900, 61, 47—63).—A continuation of the controversy with Bode (*Abstr.*, 1898, i, 682; this vol., i, 109) and Kohl (*Bot. Centr.*, 1899, 233).

T. M. L.

New Method of Methylation. By MAURICE PRUD'HOMME (*Bull. Soc. Chim.*, 1900, [iii], 23, 69—71).—The methylation of amino-groups in certain leuco-bases and colouring matters is readily effected by heating a solution of the substance with zinc dust, hydrochloric acid, and formaldehyde at 75—80°, the decolorised liquid being subsequently oxidised either by exposure to air, or by lead peroxide and acetic acid. Details are given of the application of this process to the production of methyl-violet from magenta, of a methylated rhodamine derived from *m*-diaminophenol, of methylene-blue and a greenish-blue dye from thionine, and of blue and violet colouring matters from phenosafranine. N. L.

Reactions of Methylfurfuraldehyde and Methylpentosans. By JOHN A. WIDTSOE and BERNHARD TOLLENS (*Ber.*, 1900, 33, 143—148. Compare Andrlík, this vol., i, 110).—The colour reactions of furfuraldehyde are masked in the presence of methylfurfuraldehyde. The latter is readily detected by the characteristic spectrum exhibited in the presence of hydrochloric acid. Several vegetable products, when distilled with hydrochloric acid, yield a distillate, which, when mixed with an equal volume of concentrated hydrochloric acid, shows this spectrum. Among these are : tragacanth, gum arabic, gedda gum, Brazil gum, cherry gum, *Fucus*, plane and lime tree leaves, and turf-mould. R. H. P.

Ketones of the Tropine Group. XIII. Hydroxymethylenetropinone. By RICHARD WILSTÄTTER and FRITZ IGLAUER (*Ber.*, 1900, 33, 359—365. Compare Abstr., 1899, i, 178).—*Hydroxy-*



in dry ether with amyl formate and sodium ethoxide, crystallises in aggregates of colourless plates, and melts at 128—128.5°, when it decomposes ; the aqueous and alcoholic solutions develop an intense reddish-violet coloration with ferric chloride, and reduce Fehling's solution when heated. The aqueous solution is neutral to litmus and turmeric, forming unstable salts with acids and alkalis ; the silver, gold, and platinum derivatives are indefinite, and readily decomposed. Digestion with alkalis or mineral acids eliminates formic acid. Precipitates are formed with phosphomolybdic acid, iodine in potassium iodide, or tannin ; the *picrate* is sparingly soluble in cold water, and melts at 177°, when it decomposes. The *anilide* crystallises from alcohol in aggregates of colourless needles, and melts at 158°. The *compound*, $\text{C}_9\text{H}_{15}\text{O}_2\text{N}_2\text{Cl}$, prepared by the action of hydroxylamine, followed by alcoholic hydrogen chloride, on hydroxymethylenetropinone, crystallises from alcohol in lustrous leaflets and melts at 239°, when it decomposes ; water dissolves it very readily, and the liquid reduces Fehling's solution, and develops a dark green coloration with ferric chloride.

Tropinone combines with ethyl acetate in presence of sodium ethoxide, forming acetyltropinone, the *platinichloride* of which is crystalline.

Tropinonesemicarbazone, $C_9H_{16}ON_4$, crystallises from alcohol in long, six-sided plates, and melts at $212-213^\circ$. M. O. F.

Ketones of the Tropine Group. XIV. Alkali-salts of Amino-ketones. By RICHARD WILLSTÄTTER and ADOLF BODE (*Ber.*, 1900, 33, 411—416).—When dissolved in ether or benzene, tropinone is gradually acted on by sodium or potassium, giving a metallic salt which separates as a pale yellow powder, and is completely hydrolysed by water. If stick potash is dried by heating and cooled to $130-160^\circ$, it combines completely with a tenth of its weight of fused tropinone, and the latter cannot be detected either by its smell or by turmeric paper, but is separated completely by adding water. A certain amount of a salt is also produced when an ethereal solution of tropinone is dried with stick potash or soda; a further decomposition also occurs, tropic acid being produced. Triacetoneamine, *N*-methylgranatonine (pseudopelletierine), and dimethylaminosuberone behave similarly.

When oxidised with chromic acid, *l*-ecgonine gives inactive tropinone, although in the oxidation to tropic acid both *d*- and *l*-ecgonine give *d*-tropic acid; this is readily explained if the formation of an active

intermediate, β -ketonic acid,
$$\begin{array}{c} \text{CH}_2 \cdot \text{CH} - \text{CH}_2 \\ | \quad \quad | \\ \text{NMe} \quad \text{CO} \\ | \quad \quad | \\ \text{CH}_2 \cdot \text{CH} - \text{CH} \cdot \text{CO}_2\text{H} \end{array}$$
, be assumed, since

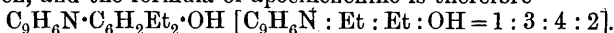
this would give an inactive tropinone by losing a mol. of carbon dioxide, but an active tropic acid by further oxidation. T. M. L.

Conversion of Cinchona-alkaloids into Derivatives of 4-Phenylquinoline. By WILHELM KOENIGS (*J. pr. Chem.*, 1900, 61, 1—46. Compare Comstock and Koenigs, *Abstr.*, 1892, 1010).—*Nitroapocinchenine*, $C_{19}H_{18}ON \cdot NO_2$, prepared by the action of nitrous acid on apocinchenine, crystallises from dilute alcohol in colourless needles, and melts with decomposition at 228° ; it does not give Liebermann's reaction. The *platinichloride*, $(C_{19}H_{18}O_3N_2)_2 \cdot H_2PtCl_6$, is an orange-yellow, crystalline powder, and is readily decomposed by water. The *ethyl ether*, prepared by the action of ethyl iodide on the insoluble silver salt, crystallises from alcohol in yellow tablets and melts at about 124° ; it is reduced by tin and hydrochloric acid to the corresponding amino-ether, which is readily soluble in alcohol and ether, and forms a *sulphate* which crystallises from hot water in golden-yellow flakes, but dissolves again in an excess of dilute sulphuric acid.

Aminoapocinchenine, $C_{19}H_{18}ON \cdot NH_2$, prepared by reducing the nitro-compound, crystallises from alcohol in almost colourless needles and melts at 220° ; it forms two series of salts, red salts with dilute acetic acid or a small amount of dilute mineral acid, and yellow salts with an excess of mineral acid. Chromic acid oxidises the base to cinchonic acid, showing that the amino-group is in the phenyl, and not in the quinoline, nucleus; in presence of dilute sulphuric acid, lead peroxide oxidises it to an intensely red solution, which becomes yellow again on adding sulphurous acid; these compounds appear to be the quinone and quinol corresponding with the original aminophenol, and the amino-group is therefore in the para-position to the hydroxyl group;

the quinol, *hydroxyapocinchenine*, was isolated in pale yellow crystals melting at 251° , but was not analysed.

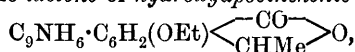
It has already been shown that the hydroxyl group in apocinchenine is adjacent to the quinoline radicle, and that the two ethyl groups occupy adjacent positions; its behaviour towards nitrous acid shows that the para-position to the hydroxyl group is occupied by hydrogen, and the formula of apocinchenine is therefore



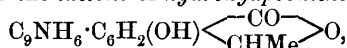
A second *nitroapocinchenine* is produced by the action of nitric acid on apocinchenine; the *hydrochloride* crystallises from hot water in colourless, glistening flakes, with $3\text{H}_2\text{O}$, and melts and decomposes at $150\text{--}160^{\circ}$; the *nitrate* and *sulphate* are also crystalline.

Tetrahydroapocinchenine, $\text{C}_{19}\text{H}_{23}\text{ON}$, prepared by reducing apocinchenine with tin and hydrochloric acid, forms a yellow, soluble resin. *Diacetyltetrahydroapocinchenine*, $\text{C}_{19}\text{H}_{21}\text{N}\text{Ac}\cdot\text{OAc}$, crystallises from alcohol in colourless needles, melts at $133\text{--}135^{\circ}$, and is readily hydrolysed by alcoholic potash or by alcoholic hydrogen bromide. Homoapocinchenine and apoquinene can be similarly reduced.

In the oxidation of apocinchenine ethyl ether with dilute nitric acid there is produced, in addition to apocinchenic acid ethyl ether, a basic compound, $\text{C}_9\text{H}_6\text{N}\cdot\text{CHO}$, which crystallises from hot water in colourless needles and melts at $101\text{--}102^{\circ}$; this is oxidised by ammoniacal silver oxide to cinchoninic acid, and is therefore 4-quinolinealdehyde; the *platinichloride* is a crystalline, orange-yellow powder. The oxidation of apocinchenine ethyl ether by manganese dioxide or lead peroxide and dilute sulphuric acid gives ketoapocinchenine ethyl ether, apocinchenic acid ethyl ether, and the lactone of hydroxyapocinchenic acid ethyl ether. *Ketoapocinchenine ethyl ether*, $\text{C}_9\text{NH}_6\cdot\text{C}_6\text{H}_2\text{Et}(\text{OEt})\cdot\text{COMe}$, crystallises from a mixture of ether and light petroleum and melts at $104\text{--}106^{\circ}$; the *platinichloride* crystallises in minute, felted needles; the *oxime* is crystalline, melts at $181\text{--}184^{\circ}$, and dissolves in dilute sodium hydroxide, but is reprecipitated by carbon dioxide; by heating with concentrated hydrobromic acid, the ketone is converted into homoapocinchenine, $\text{C}_9\text{NH}_6\cdot\text{C}_6\text{H}_3\text{Et}\cdot\text{OH}$, together with acetic acid and ethyl bromide. The *lactone* of *hydroxyapocinchenic acid ethyl ether*,



which is also produced by oxidising apocinchenic acid ethyl ether with manganese dioxide and sulphuric acid, separates from methyl or ethyl alcohol in colourless crystals and melts at $212\text{--}213^{\circ}$; hydrobromic acid converts it into the *lactone* of *hydroxyapocinchenic acid*,



which crystallises in colourless, felted needles, sinters at 260° , melts about 274° , dissolves in cold caustic alkalis, and is reprecipitated by carbon dioxide, but is hydrolysed by boiling with alkalis; hydriodic acid converts it into homoapocinchenine, $\text{C}_9\text{NH}_6\cdot\text{C}_6\text{H}_3\text{Et}\cdot\text{OH}$, carbon dioxide, and ethyl iodide, thus providing the best method for preparing homoapocinchenine; chromic acid oxidises it to cinchoninic acid; a solution of bromine in an excess of sodium hydroxide converts it almost quantitatively into quinolinephenetoleldicarboxylic acid and

carbon tetrabromide; nitric acid, alkaline permanganate, and iodine only oxidise it with difficulty. *Quinolinephenetoleedicarboxylic acid*, $C_9NH_6 \cdot C_6H_2(CO_2H)_2 \cdot OEt$, separates from alcohol in colourless crystals, melts at 236° with evolution of gas, and is only slightly soluble in water; the *hydrochloride* is completely decomposed by boiling water; the *anhydride* crystallises from ethyl acetate in minute, colourless, felted needles, melts at $210-211^\circ$, and gives a fluorescein when fused with resorcinol; chromic acid oxidises the acid to cinchoninic acid, whilst concentrated hydrobromic acid converts it into homoapocinchenic acid, $C_9NH_6 \cdot C_6H_3(OH) \cdot CO_2H$; the silver salt loses carbon dioxide when heated to $280-290^\circ$ and gives a small amount of phenetolequinoline, $C_9NH_6 \cdot C_6H_4 \cdot OEt$.

The oxidation of homoapocinchenine ethyl ether, $C_9NH_6 \cdot C_6H_3Et \cdot OEt$, with nitric acid gives an acid melting at 236° , together with a base which crystallises from dilute alcohol in white, felted needles, melts at 118° , and is found to be a *nitro*-derivative. Oxidation with manganese dioxide or lead peroxide and sulphuric acid gives ketoapocinchenine ethyl ether, homoapocinchenic acid ethyl ether, and some cinchoninic acid. *Ketohomoapocinchenine ethyl ether*, $C_9NH_6 \cdot C_6H_3(OEt) \cdot COMe$, separates from ether in colourless crystals and melts at $107-109^\circ$; the *platinichloride* crystallises in long, reddish-yellow needles and melts and decomposes at 248° . The *phenylhydrazone* separates from hot alcohol in pale yellowish crystals and melts at 220° . Iodine in presence of potassium carbonate converts the ketone partially into iodoform and homoapocinchenic acid ethyl ether, but the oxidation proceeds quantitatively when sodium hypobromite is used. *Homoapocinchenic acid ethyl ether*, $C_9NH_6 \cdot C_6H_3(OEt) \cdot CO_2H$, crystallises from alcohol, melts at $253-254^\circ$, and is only slightly soluble in water, but dissolves in hot dilute mineral acids. The *sulphate* and *platinichloride* are crystalline; hydrogen bromide converts the acid into homoapocinchenic acid, but unlike the homologue it does not lose carbon dioxide. *Homoapocinchenic acid*, $C_9NH_6 \cdot C_6H_3(OH) \cdot CO_2H$, which is also produced from quinoline phenetoleedicarboxylic acid by prolonged boiling with hydrobromic acid, is obtained as a colourless, flocculent, slightly soluble precipitate, and does not melt at 290° . On heating the silver salt with zinc dust, it is converted into phenolquinoline.

Quinolinephenetole, $C_9NH_6 \cdot C_6H_4 \cdot OEt$, crystallises from dilute alcohol in colourless needles and melts at $80-81^\circ$. The *picrate* melts at $201-202^\circ$. *Quinolinephenol*, $C_9NH_6 \cdot C_6H_4 \cdot OH$, crystallises from alcohol and melts at $207-208^\circ$; the *hydrochloride* melts at 260° , and the *hydrobromide* at 274° .

6-Aminoapocinchenine, $NH_2 \cdot C_9NH_5 \cdot C_6H_2Et_2 \cdot OH$, prepared by heating apocinchenine with zinc ammonium chloride, crystallises from alcohol and melts at $229-230^\circ$. The *hydrochloride* forms golden yellow crystals. *6-Aminoapocinchene ethyl ether*, $NH_2 \cdot C_9NH_5 \cdot C_6H_2Et_2 \cdot OEt$, crystallises from dilute alcohol and melts at $148-150^\circ$; by the action of copper powder on the diazo-compound, the base is converted into apocinchenine.

Dihydrocinchenine (Abstr., 1894, i, 392, 629) differs entirely from cinchenine in that it is not acted on by hydrobromic acid; it crystallises from dilute methyl alcohol and melts at 145° ; the *platinichloride*

crystallises from dilute hydrochloric acid in yellowish-red, microscopic tablets and melts at 265° ; the *picrate* melts at 197° . When heated with phosphoric acid, it is hydrolysed like cinchenine, but gives cincholeupone, $C_9H_{17}NO_2$, in place of meroquinine, $C_9H_{15}NO_2$, together with lepidine.
T. M. L.

Non-nitrogenous Decomposition Products of Morphine.

VI. By EDUARD VONGERICHTEN (*Ber.*, 1900, 33, 352—359. Compare Abstr., 1899, i, 649).—As a result of oxidising acetylmorphenol, the author has been led to modify his expressions for the constitution of morphenol and morphol, and now represents these compounds by the formulae $\begin{array}{c} \text{CH} \cdot \text{C}_6\text{H}_3 \\ \text{CH} \cdot \text{C}_6\text{H}_2(\text{OH}) \end{array} \text{---} \text{O}$ and $\begin{array}{c} \text{CH} \cdot \text{C}_6\text{H}_4 \\ \text{CH} \cdot \text{C}_6\text{H}_2(\text{OH})_2 \end{array}$ [OH : OH : CH = 2 : 3 : 6] respectively. He considers that the constitution of morphine is expressed by the formula advocated by Knorr (Abstr., 1899, i, 464).

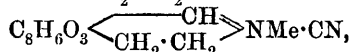
When acetylmorphenol is oxidised with chromic acid, a quinone is produced which combines with *o*-tolylenediamine, forming the *azine*, $C_{23}H_{14}O_3N_2$, crystallising from glacial acetic acid in small, yellow needles melting at 231 — 232° ; hydrochloric acid develops a bright red coloration with the azine, which forms an intensely blue solution in concentrated sulphuric acid.

Benzoylmorphenol, $C_{21}H_{12}O_3$, crystallises from glacial acetic acid in small, colourless aggregates, and melts at 123° . *Bromoacetylmorphenol*, $C_{16}H_9O_3Br$, melts at 208° .

A method is described by which morphenol can be prepared from morphine in yield amounting to nearly 40 per cent. of the calculated quantity.
M. O. F.

Cotarnine. By MARTIN FREUND [and HUGO PREUSS] (*Ber.*, 1900, 33, 380—389. Compare Hantzsch and Kalb, this vol., i, 115).—

Cyanocotarnine, $C_8H_6O_3 \begin{array}{c} \text{CH}(\text{CN}) \\ \text{CH}_2 \cdot \text{CH}_2 \end{array} \text{---} \text{NMe}$, or



prepared by the action of aqueous hydrogen cyanide on cotarnine, crystallises from alcohol in prisms which melt at 95 — 96° ; aqueous acids eliminate hydrogen cyanide, and a solution of hydrogen chloride in benzene regenerates cotarnine hydrochloride. Contrary to Hantzsch and Kalb's statement, silver nitrate and silver oxide give rise to silver cyanide. The *methiodide*, $C_{14}H_{17}O_3N_2I$, crystallises from hot water and melts at 204 — 205° , when it decomposes.

Cotarnine sulphide, $C_{24}H_{28}O_6N_2S$, obtained on passing hydrogen sulphide into a concentrated solution of cotarnine in absolute alcohol, dissolves sparingly in benzene or alcohol, being almost insoluble in ether or petroleum; it melts and decomposes at 146 — 148° . The substance is indifferent towards aqueous alkalis and alcoholic potash, but dilute acids eliminate hydrogen sulphide and regenerate cotarnine, whilst methyl iodide in hot chloroform gives rise to mercaptan and cotarnine hydriodide.

Cotarnine peroxide, $C_{24}H_{28}O_8N_2$, prepared by treating a saturated

solution of cotarnine in methyl alcohol with hydrogen peroxide, melts and intumesces at 140° ; it liberates iodine from potassium iodide, and acids eliminate hydrogen peroxide. Methyl iodide gives rise to cotarnomethine methiodide, and acetic anhydride converts it into acetyl hydrocotarnineacetic acid (Bowman, Abstr., 1887, 1056).

M. O. F.

Action of Halogens on Dimethylpiperidine. By RICHARD WILLSTÄTTER (*Ber.*, 1900, 33, 365—379. Compare Ladenburg, Abstr., 1882, 534, and Merling, Abstr., 1884, 1385).—2-Iodomethyl-1:1-

dimethylpyrrolidinium iodide, $\text{CH}_2\text{I}\cdot\text{CH}\begin{smallmatrix} \text{CH}_2-\text{CH}_2 \\ | \\ \text{NMe}_2\text{I}\cdot\text{CH}_2 \end{smallmatrix}$, prepared by heating alcoholic dimethylpiperidine with iodine, crystallises from water in long, snow-white prisms, which melt and decompose at $211-212^{\circ}$; it is precipitated from aqueous solutions by caustic soda. The bromine

compound, $\text{CH}_2\text{Br}\cdot\text{CH}\begin{smallmatrix} \text{CH}_2-\text{CH}_2 \\ | \\ \text{NMe}_2\text{Br}\cdot\text{CH}_2 \end{smallmatrix}$, crystallises from alcohol in small, four-sided plates or short prisms, and melts, evolving gas, at about 232° . Although hitherto regarded as derivatives of dimethylpiperidine, these compounds are really derived from pyrrolidine. 2-Bromomethyl-1:1-di-

methylpyrrolidinium chloride, $\text{CH}_2\text{Br}\cdot\text{CH}\begin{smallmatrix} \text{CH}_2-\text{CH}_2 \\ | \\ \text{NMe}_2\text{Cl}\cdot\text{CH}_2 \end{smallmatrix}$, obtained from the preceding compound and silver chloride, crystallises from alcohol in lustrous prisms, which melt and decompose at $224-225^{\circ}$; the *iodide* separates from water in four-sided plates, and melts at $218-219^{\circ}$.

When the bromo-bromide and iodo-iodide are heated with caustic alkalis, halogen hydride is removed, and salts of 1:1-dimethyl-2-methylenepyrrolidinium hydroxide, $\text{CH}_2\cdot\text{C}\begin{smallmatrix} \text{CH}_2-\text{CH}_2 \\ | \\ \text{NMe}_2(\text{OH})\cdot\text{CH}_2 \end{smallmatrix}$, are produced. The *iodide* is excessively soluble in cold water, and crystallises from alcohol in long, transparent prisms, which melt and decompose at 196° ; the *bromide* forms small, hygroscopic needles, and the *chloride* is deliquescent. The *platinichloride* separates from water in orange-red prisms, and gradually decomposes at about 210° ; the *aurichloride* crystallises from hot water in golden-yellow, microscopic prisms which melt and decompose at $226-227^{\circ}$.

Reduction of iodomethyldimethylpyrrolidinium iodide with zinc and concentrated hydriodic acid gives rise to 1:2-dimethylpyrrolidine methiodide (Fenner and Tafel, Abstr., 1898, i, 446). Agitating aqueous solutions of the bromo-bromide and iodo-iodide with zinc dust regenerates the base.

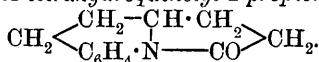
On reducing 1:1-dimethyl-2-methylenepyrrolidinium iodide with tin and hydrochloric acid, an isomeric *iodide*, $\text{C}_7\text{H}_{14}\text{NI}$, is produced, which is also unsaturated; it crystallises in thin, white, lustrous leaflets, which melt and decompose at 232° . The *platinichloride* and *aurichloride* melt at 210° and 256° respectively. M. O. F.

Optical Properties of Granatan- and Tropane-nuclei. By ANTONIO PICCININI (*Real. Accad. Lincei*, 1899, [v], 8, ii, 219—222).—The

inactive base methylgranatonine, $\text{CH}_2 \begin{array}{c} \text{CH}_2 \cdot \text{CH} \cdot \text{CH}_2 \\ | \\ \text{NMe} \\ | \\ \text{CH}_2 \cdot \text{CH} \cdot \text{CH}_2 \end{array} \text{CO}$, must be

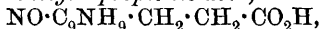
regarded as internally compensated, since, according to van't Hoff's theory, the two asymmetric carbon atoms joined to the nitrogen cannot both have a + or both a - rotation without considerable deformation of the nucleus. When the oxygen atom is replaced by H_2 and the Me by H, granatanine is obtained, and the molecule contains no asymmetric carbon atom. Similarly, tropine and ψ -tropine are seen to be internally compensated, as also are all their derivatives the molecules of which retain intact the tropine nucleus and have two equivalent asymmetric carbon atoms. T. H. P.

Tetrahydroquinolyl-2-propionic Acid. By WILHELM KOENIGS (*Ber.*, 1900, 33, 218—228).—The substance obtained by Einhorn and Sherman (*Abstr.*, 1896, i, 61) by the reduction of quinolyl-2-acrylic acid, and described by them as α -quinolylpropyl alcohol, is in reality the inner anhydride of tetrahydroquinolyl-2-propionic acid,



The corresponding acid, $\text{C}_9\text{NH}_{10} \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{CO}_2\text{H}$, is best prepared by reducing quinolylacrylic acid with sodium and alcohol, but has not been obtained crystalline; it dissolves readily in water or acids, yielding solutions which give a dark red coloration with ferric chloride or potassium dichromate. The sodium, barium, and calcium salts are readily soluble but do not crystallise, whilst the copper salt is an amorphous precipitate. When the solution of the acid is warmed, the anhydride is formed, which is only very sparingly soluble in water, and melts at $115-116^\circ$. Boiling aqueous alkalis only decompose the anhydride very slowly, a salt of the acid being produced. The anhydride gives a violet coloration with sulphuric acid and potassium dichromate, similar to that produced by strychnine, to which it is apparently closely related in constitution. When the powdered anhydride, suspended in water, is injected into a frog, no perceptible physiological action occurs.

Nitrosotetrahydroquinolyl-2-propionic acid,



is prepared from the sodium salt of the acid, and crystallises in lustrous prisms which melt and decompose at $116-117^\circ$; it forms crystalline salts, gives Liebermann's reaction, and does not yield an anhydride.

The investigation is being extended to other acids such as quinolyl-4-acrylic acid, which appears to yield a tetrahydro-derivative on reduction, but does not readily form an anhydride. A. H.

***as*-Phenylhydrazine Derivatives.** By HANS RUPE and HANS LABHARDT (*Ber.*, 1900, 33, 246—249. Compare this vol., i, 258).— α -Acetyl- β $\delta\delta$ -triphenylsemicarbazide, $\text{NHAc} \cdot \text{NPh} \cdot \text{CO} \cdot \text{NPh}_2$, obtained by heating diphenylcarbamic chloride and β -acetylphenylhydrazine in boiling cumene, separates from aromatic hydrocarbon solutions in well-defined, flattened crystals.

βδδ-Triphenylsemicarbazide, $\text{NH}_2\cdot\text{NPh}\cdot\text{CO}\cdot\text{NPh}_2$, is produced by heating the preceding compound with dilute sulphuric acid and alcohol and decomposing the resulting sulphate with sodium carbonate; the free base forms colourless crystals, and melts at 128° : the *sulphate* melts at 98° ; the *benzylidene* derivative, $\text{CHPh}\cdot\text{N}\cdot\text{NPh}\cdot\text{CO}\cdot\text{NPh}_2$ forms colourless needles and melts at $160\text{--}161^\circ$. G. T. M.

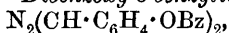
Phenylethylenehydrazine. By M. HISCHMANN (*Annalen*, 1899, 310, 156—164. Compare Burchard and Michaelis, *Abstr.*, 1890, 250).—*Ethylenebisdiphenylsemicarbazide*, $\text{C}_2\text{H}_4(\text{NPh}\cdot\text{NH}\cdot\text{CO}\cdot\text{NPh})_2$, prepared from phenylethylenehydrazine and excess of phenylcarbimide, is sparingly soluble in organic media, but crystallises from boiling alcohol in small prisms melting at $207\text{--}208^\circ$. *Ethylenebisphenylsemicarbazide*, $\text{C}_2\text{H}_4(\text{NPh}\cdot\text{NH}\cdot\text{CO}\cdot\text{NH}_2)_2$, obtained from potassium cyanate and phenylethylenehydrazine hydrochloride, melts at $237\cdot5^\circ$, and forms a crystalline *acetate* which dissociates below its melting point.

Ethyl ethylenebisphenylcarbazinate, $\text{C}_2\text{H}_4(\text{NPh}\cdot\text{NH}\cdot\text{CO}_2\text{Et})_2$, produced by the action of ethylic chlorocarbonate on phenylethylenehydrazine, separates from alcohol in small crystals and melts at $170\text{--}171^\circ$. The *methyl* ester forms lustrous leaflets and melts at $176\text{--}177^\circ$.

Ethylenecarbonylbisphenylhydrazide, $\text{C}_2\text{H}_4\left\langle\begin{smallmatrix}\text{NPh}\cdot\text{NH} \\ \text{NPh}\cdot\text{NH}\end{smallmatrix}\right\rangle\text{CO}$, obtained from carbonyl dichloride and phenylethylenehydrazine, crystallises from alcohol in lustrous, colourless needles and melts at $199\text{--}200^\circ$.

Ethylenebisphenylpicrazide, $\text{C}_2\text{H}_4[\text{NPh}\cdot\text{NH}\cdot\text{C}_6\text{H}_2(\text{NO}_2)_3]_2$, prepared from picryl chloride and phenylethylenehydrazine, melts at $202\cdot5^\circ$, when it blackens and intumesces. *Phenylhydrazinephenylethylenepicrazide*, $\text{NH}_2\text{Ph}\cdot\text{N}\cdot\text{C}_2\text{H}_4\cdot\text{NPh}\cdot\text{NH}\cdot\text{C}_6\text{H}_2(\text{NO}_2)_3$, is a bye-product in the preparation of the foregoing substance and melts at 152° , forming a *hydrochloride* which contains $4\frac{1}{2}\text{H}_2\text{O}$, and melts at $165\text{--}166^\circ$, when it decomposes. The *sulphate* and *nitrate* melt at $127\text{--}128^\circ$ and $120\text{--}121^\circ$ respectively. M. O. F.

New Aldazines and their Behaviour towards Benzoyl Chloride. By GAETANO MINUNNI and C. CARTA-SATTA (*Gazzetta*, 1899, 29, ii, 467—477).—*Dibenzoxy-o-benzylideneazaine*,



prepared by the action of benzoyl chloride on dihydroxy-o-benzylideneazaine, crystallises from benzene in glistening, yellow needles melting at $188\text{--}189^\circ$.

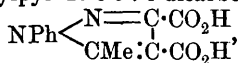
m- and p-*Nitrobenzylideneazaine*, $\text{N}_2(\text{CH}\cdot\text{C}_6\text{H}_4\cdot\text{NO}_2)_2$, obtained by the interaction of nitrobenzaldehyde and hydrazine sulphate, crystallises from benzene in glistening, yellow plates; the meta-compound melts at $194\text{--}195\cdot5^\circ$, whilst the para-form does not fuse at 260° .

T. H. P.

Replacement of the Aldehyde Group $\text{R}\cdot\text{CH}\cdot$ by Benzoyl in Hydrazine Derivatives. By GAETANO MINUNNI and C. CARTA-SATTA (*Gazzetta*, 1899, 29, ii, 377—386).—According to the conditions of experiment, the reaction between furfurylideneazaine and benzoyl chloride

gives rise to three different substances: symmetrical dibenzoylhydrazine, benzoylbenzylidenehydrazine, and *furfurylidenebenzoylhydrazine*, $C_4H_3O \cdot CH:N \cdot NHBz$, which separates from alcohol in yellowish, flattened needles melting at $178-179^\circ$. T. H. P.

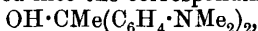
So-called Isopyrazole Derivatives. By FRIEDRICH STOLZ (*Ber.* 1900, 33, 262—265. Compare this vol., i, 56).—On heating Bülow and Schlesinger's "1-phenyl-3-methylisopyrazole-4:5-dicarboxylic acid," carbon dioxide is evolved and Claisen's 1-phenyl-5-methylpyrazole-4-carboxylic acid, $CO_2H \cdot C \begin{smallmatrix} \swarrow CMe \cdot NPh \\ \searrow CH=N \end{smallmatrix}$, is obtained (Abstr., 1894, i, 345, and 1897, i, 440); this indicates that the dicarboxylic acid is in reality 1-phenyl-5-methylpyrazole-3:4-dicarboxylic acid,



and therefore "1-phenyl-3-methylisopyrazole" is identical with 1-phenyl-5-methylpyrazole.

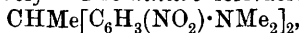
The discrepancy existing between the melting point of Knorr and Laubmann's dicarboxylic acid (m. p. 198° , Abstr., 1889, 409) and that of Bülow and Schlesinger's acid (m. p. 247°) is due to the presence of an isomeride in the former preparation, the substance being obtained by the oxidation of 1-phenyl-3:5-dimethylpyrazole-4-carboxylic acid, a process which might give rise to two dicarboxylic acids according as to which of the methyl groups undergoes oxidation. The *acid ester*, $C_{14}H_{14}N_2O_4$, the first product of the hydrolysis of diethyl benzeneazodiacetylsuccinate, crystallises from alcohol in needles and melts at 185° ; on further treatment with alcoholic sulphuric acid, this compound yields the free dicarboxylic acid (m. p. 247°). G. T. M.

Derivatives of the Leuco-base, $C_{18}H_{24}N_2$. By AUGUSTE TRILLAT (*Bull. Soc. Chim.*, 1899, [iii], 23, 20—24. Compare Abstr., 1899, i, 615).—When *as*-tetramethyldiaminodiphenylethane, $CHMe(C_6H_4 \cdot NMe_2)_2$, is dissolved in anhydrous acetic acid and treated with lead peroxide in the cold, it is converted into the corresponding *carbinol*,



which was obtained as a brown mass, soluble in acids with the production of a blue solution. The blue colour is destroyed by heating with lead peroxide and acetic acid, and cannot be made to reappear, whereas the homologous tetramethyldiaminodiphenylcarbinol, $OH \cdot CH(C_6H_4 \cdot NMe_2)_2$, when similarly treated, is first decolorised and then assumes an intense colour again on further heating. As might be expected from its constitution, the new carbinol furnishes no colouring matters when heated with aniline, dimethylaniline, or phenols in the presence of sulphuric acid. *Tetramethyldiaminodiphenylethane dihydrochloride* is a white, crystalline substance which melts and decomposes at 225° and is soluble in water or alcohol, but almost insoluble in acetone; the *acid sulphate*, a hygroscopic, crystalline compound, melts at $188-189^\circ$; the *acetate* crystallises in long needles which redden on exposure to the air; the *phosphate*, *oxalate*, and *tartrate* have also been prepared. The base readily combines with ethyl bromide to form a compound, $C_{18}H_{24}N_2 \cdot 2EtBr$, which crystallises

in white scales melting and decomposing at 224—225° and is soluble in water or alcohol; the corresponding *ethiodide* derivative crystallises in large, white needles, melts and decomposes at 228—230°, and is soluble in water or alcohol, slightly so in acetone. Similar compounds are formed with methyl bromide and iodide. When treated with bromine or iodine in acetic acid solution, the base yields amorphous, unstable compounds of the composition $C_{18}H_{21}Br_3N_2$ and $C_{18}H_{21}I_3N_2$ respectively. The *dinitro-derivative*,



obtained by the action of cold nitric acid, crystallises in small, pale yellow prisms melting at 195—196°; when reduced with zinc dust and acetic acid, it yields a substance which gives a splendid red coloration on oxidation.

N. L.

Naphthylated Benzidines. By VICTOR MERZ and H. STRASSER (*J. pr. Chem.*, [ii], 60, 545—565. Compare Abstr., 1899, i, 917).—A mixture of α -naphthyl-*m*-phenylenediamine and dinaphthyl-*m*-phenylenediamine is obtained when equal quantities of pure α -naphthol and *m*-phenylenediamine are heated for some 20 hours as previously recommended for the β -compound. Any excess of naphthol is removed by heating the mixture to 370°; the mono- and di-naphthyl compounds are best separated by the aid of boiling dilute hydrochloric acid, which dissolves out the mono-derivative in the form of its hydrochloride whereas the dinaphthyl compound remains undissolved. α -Naphthyl-*m*-phenylenediamine, $C_{16}H_{14}N_2$, distils at 275—280° under 15 mm. pressure, and on cooling solidifies to a yellowish-red, vitreous mass; when dissolved in benzene and precipitated by light petroleum, nodular aggregates consisting of minute, colourless needles are obtained. It melts at 94·5—95°, is readily soluble in hot alcohol, ether, or benzene, and to some extent in water; when kept, it turns first red and finally violet-grey. The *hydrochloride*, $C_{16}H_{14}N_2 \cdot HCl$, crystallises in small, colourless needles, and the *sulphate* in colourless plates.

When *m*-phenylenediamine is heated with a large excess of naphthol (4 mols.), the chief products are the mono- and di-naphthyl compounds and α -naphthyl oxide. α -Dinaphthyl-*m*-phenylenediamine, $C_{26}H_{20}N_2$, distils at 345° under 6 mm. pressure and solidifies to a pale red, vitreous mass; it crystallises from a mixture of benzene and alcohol in small, greyish needles melting at 137·5—138°, and is readily soluble in benzene at 19° (1 part in 19·3). This compound appears to exist in a second modification, as when the crude condensation product is crystallised from hot alcohol needles melting at 101·5—102° are obtained, which then solidify and melt a second time at 137·5—138°. A similar transformation occurs when the compound of low melting point is boiled with alcohol.

α -Naphthyl-*p*-phenylenediamine (57—67 per cent.) is formed together with the dinaphthylated base (10—12 per cent.) when the constituents are heated according to the method previously described; it crystallises from benzene and light petroleum in colourless plates, melts at 80·5—81°, distils at 275—280° under 12 mm. pressure, and is readily soluble in the ordinary organic solvents. The *hydrochloride* and *sulphate* crystallise in colourless plates. In moderately dilute acid

solution, the hydrochloride gives a dark, flocculent precipitate with ferric chloride; in extremely dilute solutions, an intense bluish-violet colour is developed. *α-Dinaphthyl-p-phenylenediamine*, obtained in larger quantities when an excess of the naphthol is employed, crystallises from hot benzene in the form of flat, colourless needles, melts at 205·5°, distils at 355° under 5 mm. pressure, and dissolves in 319 parts of benzene at 19°.

αβ-Dinaphthyl-m-phenylenediamine obtained from *α*-naphthyl-m-phenylenediamine and *β*-naphthol, distils at 355—358° under 6—7 mm. pressure and crystallises in needles melting at 140°. *αβ-Dinaphthyl-p-phenylenediamine* crystallises from hot benzene in glistening plates, melts at 204°, distils at 370—375° under 9 mm. pressure, and is completely decomposed when heated for 6 hours at 200° with 20 per cent. hydrochloric acid. Both compounds exhibit fluorescence in benzene solution. J. J. S.

Wandering of the Orthoquinonoid Double Linking in Azonium Compounds. (II.) By FRIEDRICH KEHRMANN (*Ber.*, 1900, 33, 395—411. Compare Abstr., 1898, i, 439).—I. [With M. STOFFEL.]—**Nitro- and Amino-flavindulines.** *2-Nitroflavinduline chloride*, $\text{C}_6\text{H}_4 \cdot \text{C} \begin{array}{l} \text{---} \text{N} \\ | \\ \text{C} \cdot \text{NPhCl} \end{array} > \text{C}_6\text{H}_3 \cdot \text{NO}_2$, prepared by the action of phenanthraquinone on the hydrochloride of *p*-nitro-*o*-aminodiphenylamine, separates from water in very soluble, reddish-brown needles; the *nitrate* crystallises from alcohol in transparent, reddish-brown prisms, and the *platinichloride* and *dichromate* form yellowish-red crystals. On adding sodium hydroxide, ammonia, or aniline to an alcoholic solution of the chloride, it gradually becomes clear-yellow as the base passes into the carbinol form (Abstr., 1899, i, 506; compare Hantzsch and Kalb, this vol., i, 113).

2-Aminoflavinduline hydrochloride, prepared by reducing the nitro-compound with tin and hydrochloric acid, oxidising the tin salt of the leuco-base with ferric chloride, and decomposing the tin salt of the colour-base by extracting with dilute alcohol, crystallises from water in violet-black needles, and from alcohol in short, stout, many-faced prisms; the *nitrate* is insoluble in water, but crystallises from alcohol in violet-black flakes with a metallic lustre; the *platinichloride* and the *dichromate* are blue-black or green-black, crystalline powders.

2-Acetylaminoflavinduline chloride, crystallises from alcohol in brownish-red needles with a greenish, metallic lustre; the *nitrate* is insoluble in water, but crystallises from alcohol in red prisms; the *platinichloride* and the *dichromate* are red, crystalline powders.

2:3-Diaminoflavinduline chloride, prepared by the action of ammonia on 2-aminoflavinduline chloride, is a red salt which is slightly soluble in hot water, but separates completely on cooling.

2-Amino-3-methylaminoflavinduline chloride, prepared similarly from methylamine and 2-aminoflavinduline chloride, separates from hot water in dark violet needles with a green, metallic lustre; the *nitrate* crystallises from alcohol in reddish-violet needles with a green, metallic lustre.

2-Amino-3-dimethylaminoflavinduline chloride can be obtained in long

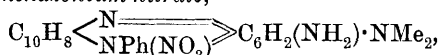
needles with a green lustre by crystallising from a mixture of alcohol and ether; the insoluble *nitrate* crystallises from alcohol in flaky crystals with a green lustre; the *platinichloride* is a violet, and the *dichromate* a green, crystalline powder.

2-Amino-3-anilino β -naphtholamine hydrochloride separates from dilute alcohol in large, flaky crystals; the *base* separates from dilute alcohol in reddish-brown flakes with a metallic lustre, and melts and decomposes at 290°. Phenylphenanthraquinone hydrochloride,

$C_{14}H_8 \begin{smallmatrix} \text{N} \\ \text{NPh} \end{smallmatrix} \begin{smallmatrix} \text{=N} \\ \text{=N} \end{smallmatrix} C_6H_2 \begin{smallmatrix} \text{NH} \\ \text{N} \end{smallmatrix} C_6H_4 \cdot HCl$, prepared by fusing the preceding chloride with *o*-phenylenediamine hydrochloride and benzoic acid, crystallises from alcohol in large needles with a green lustre; on adding ammonia to an alcoholic solution of the chloride, the *base* separates in minute, golden flakes.

II. [With CH. VALENCIEN.]—Behaviour of 2-Nitro- and 2-Amino-naphthaphenazonium Salts towards Amines. By the action of ammonia on 2-nitrophenylnaphthaphenazonium chloride (Abstr., 1898, i, 155), an amino-group is introduced into the naphthalene nucleus, giving rise to 2-nitrosinduline chloride. Similarly, aniline gives a chloride and base identical with those prepared from 4-anilino- β -naphthaquinone and nitrophenyl-*o*-phenylenediamine.

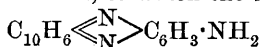
In the corresponding amino-compounds, substitution takes place in the benzene, and not in the naphthalene nucleus; this is regarded as an indication that the double bonds occupy a different position in the amino-compounds, and the latter are regarded as benzoquinone, and not naphthaquinone derivatives. 2-Amino-3-dimethylamino-5-phenylnaphthaphenazonium nitrate,



crystallises from alcohol in metallic green needles, and dissolves in water or alcohol to magenta-red solutions which become violet-blue on adding much dilute acid, owing to the formation of di-acid salts; the *dichromate* forms a dark, violet-brown, insoluble crystal powder; the *platinichloride* is a dark-brown, insoluble, crystalline powder, with a metallic lustre. 2-Amino-3-anilinophenylnaphthaphenazonium-5-

chloride, $C_{10}H_8 \begin{smallmatrix} \text{N} \\ \text{NPhCl} \end{smallmatrix} \begin{smallmatrix} \text{=N} \\ \text{=N} \end{smallmatrix} C_6H_2(NH_2) \cdot NHPh$, separates from alcohol in metallic green crystals; the (anhydride-) *base* forms reddish-brown crystals with a metallic green lustre. The structure of these substances is proved by their close resemblance to the analogous compounds previously described (Abstr., 1898, i, 439; 1899, i, 238) and by the fact that they give fluorindines when fused with benzoic acid and *o*-phenylenediamine.

2-Amino-5-phenylnaphthaphenazonium chloride exists in two modifications. The stable form, to which the formula $C_{10}H_6 \begin{smallmatrix} \text{N} \\ \text{N} \end{smallmatrix} \begin{smallmatrix} \text{=N} \\ \text{=N} \end{smallmatrix} C_6H_3 \cdot NH_2$ is assigned, dissolves in water to a dirty-violet, and in alcohol to a blue solution. The labile form, to which the formula



is assigned, is prepared by cautious reduction of the nitro-compound,

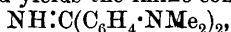
and dissolves in water or alcohol to a red-violet solution; on boiling the alcoholic solution, it passes to the stable blue form, and in a similar manner, when treated with dimethylamine gives the stable substitution product already described. The stable *acetyl* derivative, prepared from the tin salt of either modification of the chloride, crystallises from hot water in minute, red needles; the *acetylamino-nitrate* is only slightly soluble, and forms minute, red, felted needles.

T. M. L.

Transformation of Colour-bases into Pseudo-ammonium Hydroxides, Cyanides, and Sulphonic Acids. By ARTHUR HANTZSCH and G. OSSWALD (*Ber.*, 1900, 33, 278—317).—On adding one equivalent of sodium hydroxide to an aqueous solution of a diphenyl- or triphenyl-methane colour-base of the ammonium hydroxide type, $\text{:C:C} \begin{smallmatrix} \text{CH:CH} \\ \text{CH:CH} \end{smallmatrix} \text{>C:NR}'_2 \cdot \text{OH}$, the true base is initially formed, but

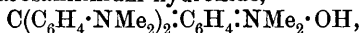
is rapidly converted into a colourless pseudo-base of the carbinol type, $\text{:C(OH)C}_6\text{H}_4 \cdot \text{NR}'_2$; the true base is soluble in water and is highly dissociated in solution, whilst the pseudo-base is insoluble and non-dissociating. The transformation of the true into the pseudo-base can therefore be studied by observing the decrease in electrical conductivity of the solution (compare Abstr., 1899, i, 400, and this vol., i, 113).

In the case of the auramine base, $\text{NMe}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{C(NH}_2\text{)} \cdot \text{C}_6\text{H}_4 \cdot \text{NMe}_2 \cdot \text{OH}$, the pseudo-base, $\text{NH}_2 \cdot \text{C(C}_6\text{H}_4 \cdot \text{NMe}_2)_2 \cdot \text{OH}$, is first formed, but this immediately loses water and yields the imino-compound,



as a precipitate; the initial conductivity on liberating the base is therefore low, over 3/4 of the pseudo-base separating instantaneously in the form of the anhydride.

Hexamethylpararosaniminium hydroxide,



liberated from "crystal violet" hydrochloride by adding one equivalent of sodium hydroxide, has μ_∞ 223.4 at 25°, and 128.2 at 0°; after being in contact with water for 5 hours at 25°, it is nearly completely converted into hexamethyltriaminotriphenylcarbinol ("crystal violet" leuco-hydroxide), $\text{OH} \cdot \text{C(C}_6\text{H}_4 \cdot \text{NMe}_2)_3$. The conversion of the "brilliant green" base, $\text{NEt}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{CPh:C}_6\text{H}_4 \cdot \text{NEt}_2 \cdot \text{OH}$, into "brilliant green" leuco-hydroxide, $\text{OH} \cdot \text{CPh(C}_6\text{H}_4 \cdot \text{NEt}_2)_2$, takes place even more rapidly. On adding sodium hydroxide to a solution of pararosanine hydrochloride, the strongly dissociating base, $\text{C(C}_6\text{H}_4 \cdot \text{NMe}_2)_2 \cdot \text{C}_6\text{H}_4 \cdot \text{NH}_2 \cdot \text{OH}$, is initially formed, but after 3 hours at 25° this is completely converted into the leuco-hydroxide (triaminotriphenyl carbinol), $\text{OH} \cdot \text{C(C}_6\text{H}_4 \cdot \text{NH}_2)_3$; it is noteworthy that the true base shows no tendency to form the imino-base, $\text{C(C}_6\text{H}_4 \cdot \text{NMe}_2)_2 \cdot \text{C}_6\text{H}_4 \cdot \text{NH}$, by loss of water. Curves are given showing the rate of transformation at 0° and 25° of the true into the pseudo-bases in all the cases dealt with.

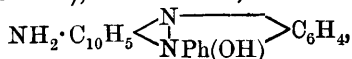
On adding sodium cyanide (1 mol.) to an aqueous solution of pararosanine hydrochloride, the true cyanide is initially formed, but after 10 minutes at 25° or 1 hour at 0°, the pseudo- or leuco-cyanide, $\text{CN} \cdot \text{C(C}_6\text{H}_4 \cdot \text{NH}_2)_3$, begins to separate, the electrical conductivity

falling simultaneously; a curve is given showing the rate of this change. The *pseudo-cyanide*, $\text{CN} \cdot \text{C}(\text{C}_6\text{H}_4 \cdot \text{NMe}_2)_3$ (*hexamethyltri-aminotriphenylacetone nitrile*), prepared similarly from "crystal violet," crystallises from alcohol in colourless, cruciform aggregates, and from benzene in slightly bluish needles, which, on heating, become first green, then brown, and finally melt and decompose at $288-290^\circ$; the *tri-hydrochloride*, $\text{C}_{26}\text{H}_{33}\text{N}_4\text{Cl}_3$, forms beautiful, colourless crystals, the *mercuric chloride* derivative, $\text{CN} \cdot \text{C}(\text{C}_6\text{H}_4 \cdot \text{NMe}_2)_3 \cdot 3\text{HgCl}_2$, a white powder, and the *hydriodide*, slender, colourless needles, which blacken at 180° and decompose at 190° ; with iodine, the latter yields the *periodide*, $\text{C}_{26}\text{H}_{33}\text{N}_4\text{I}_5$, which separates from alcohol in dark brown crystals and melts at $183-184^\circ$. Attempts to hydrolyse the *pseudo-cyanide* to the corresponding amide or carboxylic acid gave no result.

The *pseudo-cyanide*, $\text{CN} \cdot \text{CPh}(\text{C}_6\text{H}_4 \cdot \text{NMe}_2)_2$, derived from "malachite green," separates from a mixture of benzene and ethyl acetate in beautiful, colourless crystals, and melts and decomposes at 176° . "*Brilliant green*" *pseudo-cyanide*, $\text{CN} \cdot \text{CPh}(\text{C}_6\text{H}_4 \cdot \text{NEt}_2)_2$, prepared similarly, forms white crystals, melts at 160° , and yields a *dihydrochloride*, $\text{C}_{28}\text{H}_{35}\text{N}_3\text{Cl}_2$, which separates in nearly colourless crystals. It is noteworthy that none of the *pseudo-cyanides* described can be prepared by the interaction of hydrocyanic acid with the corresponding *pseudo-bases*.

"*Brilliant green*" *leucosulphonic acid*, $\text{SO}_3\text{H} \cdot \text{CPh}(\text{C}_6\text{H}_4 \cdot \text{NMe}_2)_2$, prepared by the action of sulphur dioxide on "brilliant green" leuco-hydroxide dissolved in ether, is colourless, somewhat unstable, and melts at 154° ; the more stable *sulphate*, $\text{SO}_3\text{H} \cdot \text{CPh}(\text{C}_6\text{H}_4 \cdot \text{NEt}_2)_2 \cdot \text{H}_2\text{SO}_4$, prepared similarly from the sulphate of the colour base, crystallises from water in aggregates of colourless needles and melts and decomposes at 137° . From "crystal violet," no analogous compound can be obtained, but pararosaniline hydrochloride yields the *leucosulphonic derivative*, $\text{SO}_3\text{H} \cdot \text{C}(\text{C}_6\text{H}_4 \cdot \text{NH}_2)_3$, $\text{HCl} + 2\text{H}_2\text{O}$, as a white, microcrystalline mass. Mineral acids in the cold, and aqueous alkalis on warming, remove sulphur dioxide from these *sulphonic derivatives*, the latter in this respect being comparable with the *syn-diazosulphonates*.

On adding sodium hydroxide to rosinduline hydrochloride (μ_∞ 225.3 at 25° , 129.9 at 0°), the true base,



initially formed, is almost instantaneously converted, by loss of water, into the insoluble *pseudo-base*, $\text{NH} \cdot \text{C}_{10}\text{H}_5 \left\langle \begin{array}{c} \text{N} \\ | \\ \text{NPh} \end{array} \right\rangle \text{C}_6\text{H}_4$. With 1 mol. of

sodium hydroxide, rosindone chloride, $\text{C}_{10}\text{H}_5\text{Cl} \left\langle \begin{array}{c} \text{N} \\ | \\ \text{NPhCl} \end{array} \right\rangle \text{C}_6\text{H}_4$, yields the stable, strongly dissociating, *true base*, chloronaphthaphenazonium hydroxide, $\text{C}_{10}\text{H}_5\text{Cl} \left\langle \begin{array}{c} \text{N} \\ | \\ \text{NPh}(\text{OH}) \end{array} \right\rangle \text{C}_6\text{H}_4$, whilst with 2 mols., the *base*,

$\text{OH} \cdot \text{C}_{10}\text{H}_5 \left\langle \begin{array}{c} \text{N} \\ | \\ \text{NPh}(\text{OH}) \end{array} \right\rangle \text{C}_6\text{H}_4$, appears to be formed, but gradually

decomposes at 25° , and yields rosindone, $\text{O} \cdot \text{C}_{10}\text{H}_5 \left\langle \begin{array}{c} \text{N} \\ | \\ \text{NPh} \end{array} \right\rangle \text{C}_6\text{H}_4$.

Flavindulinium hydroxide, liberated from the strongly dissociating chloride, is almost instantaneously converted into an insoluble pseudo-base, whilst on the other hand, the bases liberated from the hydrochlorides of phenosafranine and methylene-blue are perfectly stable in contact with water at 0° , and do not yield pseudo-forms; at 25° , water brings about secondary decomposition.

W. A. D.

Constitution of Auramine. By ALFRED STOCK (*Ber.*, 1900, 33, 318—320. Compare Hantzsch and Osswald, preceding abstract).—Phenylmethyllauramine hydrochloride, prepared by heating tetramethyldiaminobenzophenone hydrochloride with methylaniline, or from dimethylaminobenzomethylaniline and dimethylaniline (German Patent, 44,077), combines with ammonium thiocyanate to form a red, crystalline *thiocyanate*, $C_{25}H_{28}N_4S$, which, on hydrolysis with alkalis, yields methylaniline and the corresponding ketone, and with potassium cyanide gives rise to *phenylmethyllauramine hydrocyanide*, $CN \cdot C(C_6H_4 \cdot NMe_2)_2 \cdot NMePh$; this separates from ether in large, slightly yellow-coloured crystals, melts at 99° , and when warmed with alcohol gives an equilibrium with the yellowish-red, tautomeric form, $NMe_2 \cdot C_6H_4 \cdot C(NMePh) : C_6H_4 \cdot NMe_2 \cdot CN$; on adding sulphur to the solution, the latter form is converted into the thiocyanate, and a further quantity of the red hydrocyanide is then formed, which is similarly removed. From these facts, Graebe's doubts (*Abstr.*, 1899, i, 702) as to the existence of phenylmethyllauramine, and his arguments in favour of the imine formula for auramine, appear to be no longer tenable.

W. A. D.

Synthesis of Phenylhydroxytriazoles. By HANS RUPE and HANS LABHARDT (*Ber.*, 1900, 33, 233—246. Compare *Abstr.*, 1899, i, 356).—When the aliphatic β -acylphenylhydrazines are treated with carbamic chloride, the group $CO \cdot NH_2$ is introduced into the molecule; further condensation then takes place with elimination of water, and a hydroxytriazole is produced.

1-Phenyl-3-methyl-5-ketotriazole-4-carbamide, $NH_2 \cdot CO \cdot N < \begin{matrix} CMe \cdot N \\ CO - NPh \end{matrix}$, prepared by mixing carbamic chloride with β -acetylphenylhydrazine suspended in dry benzene, crystallises from alcohol in colourless needles melting at 154 — 155° . A small quantity of phenylmethyloxydiazole (*Abstr.*, 1890, 1440) may be isolated from the benzene mother liquors; this compound is produced by the interaction of between β -acetylphenylhydrazine and the carbonyl chloride present in the carbamic chloride. The action of carbonyl chloride on other β -acylphenylhydrazines in boiling benzene gives rise to homologous diazoles.

1-Phenyl-3-benzoyloxydiazolone, obtained from α -acetyl- $\alpha\beta$ -diphenylhydrazine, crystallises in leaflets melting at 68° ; it is readily hydrolysed by acids or alkalis.

5-Hydroxy-1-phenyl-3-methyltriazole, produced by hydrolysing the preceding carbamide, crystallises in leaflets melting at 163 — 164° , and is identical with the compound obtained by Andreocci (*Abstr.*, 1890, 889), from acetylurethane and phenylhydrazine.

1-Phenyl-5-ketotriazole-4-carbamide, $\text{NH}_2 \cdot \text{CO} \cdot \text{N} \begin{smallmatrix} \text{CH} \cdot \text{N} \\ \text{CO} \cdot \text{NPh} \end{smallmatrix}$, obtained by the action of carbamic chloride on β -formylphenylhydrazine, melts at $163\text{--}164^\circ$; it is readily hydrolysed into 5-hydroxy-1-phenyltriazole, $\text{CH} \begin{smallmatrix} \text{N} \cdot \text{NPh} \\ \text{N} \cdot \text{C} \cdot \text{OH} \end{smallmatrix}$, which crystallises in colourless leaflets or prisms, melts at $179\text{--}181^\circ$, and resembles its methyl homologue in its solubility in organic solvents and in solutions of the alkalis.

5-Acetoxy-1-phenyltriazole, produced by the action of acetic anhydride and anhydrous sodium acetate on the preceding compound, crystallises in colourless needles; the acetyl group is readily removed with the formation of the original triazole.

1-Phenyl-3-ethyl-5-ketotriazole-4-carbamide, $\text{NH}_2 \cdot \text{CO} \cdot \text{N} \begin{smallmatrix} \text{CEt} \cdot \text{N} \\ \text{CO} \cdot \text{NPh} \end{smallmatrix}$, from carbamic chloride and β -propionylphenylhydrazine, melts at 148° , and resembles its lower homologues.

5-Hydroxy-1-phenyl-3-ethyltriazole, $\text{CEt} \begin{smallmatrix} \text{N} \cdot \text{C} \cdot \text{OH} \\ \text{N} \cdot \text{NPh} \end{smallmatrix}$, produced from the preceding compound by alkaline hydrolysis, crystallises in white needles, and resembles its homologues; the *acetoxy*-derivative, obtained by the action of acetic anhydride and excess of anhydrous sodium acetate, crystallises in radiate aggregates of colourless needles and melts at $62\text{--}63^\circ$.

1-Phenyl-4-methyl-3-ethyl-5-ketotriazole, $\text{NMe} \begin{smallmatrix} \text{CEt} \cdot \text{N} \\ \text{CO} \cdot \text{NPh} \end{smallmatrix}$, prepared by heating 5-hydroxy-1-phenyl-3-ethyltriazole with sodium methoxide and methyl iodide in methyl alcohol solution at 100° , crystallises from dilute alcohol in prisms melting at $77\text{--}78^\circ$; it is insoluble in alkalis and not affected by hydrochloric acid.

Carbamic chloride has no action on β -benzoylphenylhydrazine, but the carbonyl chloride present in the impure reagent gives rise to diphenyloxydiazolone.

5-Hydroxy-1-phenyl-3-benzyltriazole, $\text{CH}_2\text{Ph} \cdot \text{C} \begin{smallmatrix} \text{N} \cdot \text{NPh} \\ \text{N} \cdot \text{C} \cdot \text{OH} \end{smallmatrix}$, obtained by the action of carbamic chloride on α -acetyl- $\alpha\beta$ -diphenylhydrazine, crystallises from alcohol in lustrous, colourless leaflets and melts at 187° ; the intermediate carbamide could not be isolated in this case. The triazole is very stable towards acids and alkalis.

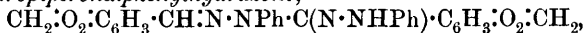
When carbamic chloride interacts with phenylsemicarbazide, 3:5-dihydroxy-1-phenyltriazole is produced (Pinner, Abstr., 1888, 687).

G. T. M.

Dipiperonaldiphenylhydrotetrazone and its Isomeric Transformations. By GAETANO MINUNNI (*Gazzetta*, 1899, 29, ii, 420—434). —Dipiperonaldiphenylhydrotetrazone, $\text{N}_2\text{Ph}_2(\text{N} \cdot \text{CH} \cdot \text{C}_6\text{H}_3 \cdot \text{O}_2 \cdot \text{CH}_2)_2$, prepared by oxidising piperonalphenylhydrazone in ethereal solution by means either of amyl nitrite or mercuric oxide, separates from benzene in small, yellow prisms or leaflets, soluble in acetone or chloroform. It dissolves readily in concentrated sulphuric acid, forming a

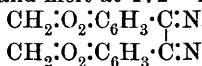
violet coloration which rapidly turns brown. When heated slowly, it softens at 147° and melts at 148 – 149° or at 150 – 152° , but with quicker heating turns brown at 155° and melts at 156 – 157° . The limpid, fused mass does not crystallise on cooling. Benzoyl chloride or alcoholic potash converts it into piperil- β -osazone, prepared by Biltz and Wienands (Abstr., 1899, i, 911); when heated with an excess of benzoyl chloride, piperil- β -osazone gives rise to a small quantity of a compound which separates from benzene by the addition of alcohol in almost white flocks melting at above 240° .

Dehydropiperonalphenylhydrazone,



obtained by the action of heat on dipiperonaldiphenylhydrotetrazone, separates from benzene on the addition of alcohol in reddish-brown granules which darken at 170° and melt at 172 – 173° .

Phenyldipiperonalosotriazone,

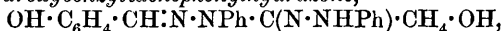


prepared by the dry distillation of piperil- β -osazone, separates from dilute alcohol in white, microscopic crystals melting at 153 – 155° . T. H. P.

Oxidation of Cinnamaldehydephenylhydrazone. By GAETANO MINUNNI and GIOVANNI ORTOLEVA (*Gazzetta*, 1899, 29, ii, 434–436).—By oxidising cinnamaldehydephenylhydrazone in chloroform solution by means of mercuric oxide, *dehydrocinnamaldehydephenylhydrazone* (?), $\text{CHPh:CH:CH:N}\cdot\text{NPh}\cdot\text{C(N}\cdot\text{NPh)}\cdot\text{CH:CHPh}$, is obtained in small quantity; it separates from benzene on the addition of alcohol in minute, yellow crystals which soften at 200° and melt at 203 – 204° .

T. H. P.

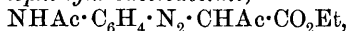
Oxidation of Salicylaldehydephenylhydrazone. By GAETANO MINUNNI and C. CARTA-SATTA (*Gazzetta*, 1899, 29, ii, 437–443).—On oxidising salicylaldehydephenylhydrazone by means of amyl nitrite, *dehydro-o-hydroxybenzylidenephenylhydrazone*,



is obtained; it is soluble in benzene, from which it is deposited, on adding alcohol, in yellowish flocks of minute, acicular crystals which melt and evolve gas at 210° . Sulphuric acid dissolves it with the formation of a greenish solution. Its *tribenzoyl* derivative, $\text{C}_{26}\text{H}_{19}\text{O}_2\text{N}_4\text{Bz}_3$, separates from its benzene solution on the addition of alcohol either slowly in the form of large, yellowish, prismatic crystals, or quickly as slender needles melting at 156 – 157° to a black liquid. T. H. P.

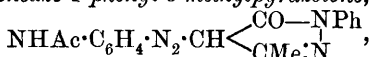
Benzylidene Derivatives of Triaminodiphenylamine. By MAX GRONEBERG (*Ber.*, 1900, 33, 215–218).—4:2':4'-*Tribenzylidenetriaminodiphenylamine*, $\text{CHPh:N}\cdot\text{C}_6\text{H}_4\cdot\text{NH}\cdot\text{C}_6\text{H}_3(\text{N:CHPh})_2$, is obtained by the action of benzaldehyde on 4:2':4'-triaminodiphenylamine and decomposes when heated. When treated with dilute acids, benzaldehyde is regenerated to some extent, and a light grey, amorphous substance obtained which melts at 122 – 124° to a brown syrup, and has the composition of a *sesquibenzylidenetriaminodiphenylamine*, $\text{CHPh}[\text{NH}\cdot\text{C}_6\text{H}_4\cdot\text{NH}\cdot\text{C}_6\text{H}_3(\text{NH}_2)\cdot\text{N:CHPh}]_2$. The *oxalate* is a light green, bulky powder. A. H.

Aliphatic-aromatic Azo- and Tetrazo-derivatives of *p*-Phenylenediamine. By CARL BÜLOW (*Ber.*, 1900, 33, 187—199).—*Ethyl-α-p-acetaminophenylazoacetoacetate*,



prepared by combining *p*-acetaminodiazobenzene chloride with ethyl acetoacetate, crystallises from dilute alcohol in stout, yellow needles, melts at 148°, and on warming with aqueous ammonia yields the corresponding *amide*, $\text{C}_{11}\text{H}_{12}\text{O}_2\text{N}_3 \cdot \text{CO} \cdot \text{NH}_2$, which forms yellow, lustrous needles, and melts and decomposes at 228—229°; methylamine gives rise to the *methylamide*, $\text{C}_{11}\text{H}_{12}\text{O}_2\text{N}_3 \cdot \text{CO} \cdot \text{NHMe}$, which crystallises from alcohol or glacial acetic acid in sulphur-yellow needles.

4-*p*-Acetaminobenzeneazo-1-phenyl-3-methylpyrazolone,



prepared by adding phenylhydrazine acetate to a boiling alcoholic solution of ethyl *α-p*-acetaminophenylazoacetoacetate, crystallises from alcohol in slender, yellowish-red, felted needles and melts at 222—223°; on hydrolysis with either boiling aqueous sodium hydroxide or 10 per cent. alcoholic hydrochloric acid, it yields the corresponding *base*, which crystallises from alcohol in brownish-red, highly lustrous prisms, melts at 206—207°, and yields a *benzoyl* derivative crystallising in lustrous, orange-yellow leaflets and melting at 238°. On combining the diazo-chloride of the base with ethyl acetoacetate, the *tetrazo*-compound

$\text{CO}_2\text{Et} \cdot \text{CHAc} \cdot \text{N}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{N}_2 \cdot \text{CH} \begin{array}{l} \text{CO—NPh} \\ \text{CMe:N} \end{array}$, is obtained; this separates from alcohol in vermilion crystals, melts at 181—182°, and, with phenylhydrazine, yields *p-bis-1-phenyl-3-methylpyrazoloneazobenzene*, $\text{C}_6\text{H}_4 \left(\text{N:N} \cdot \text{CH} \begin{array}{l} \text{CO—NPh} \\ \text{CMe:N} \end{array} \right)_2$, which crystallises in red needles and does not melt at 280°.

All the compounds described possess feebly acid properties, dissolving unchanged in warm dilute aqueous alkalis to yield coloured solutions; this behaviour is probably due to the $\cdot\text{CH}$ group contiguous to the carbonyl radicle.

W. A. D.

Polymerisation Products from Ethyl Diazoacetate. By ARTHUR HANTZSCH and OSWALD SILBERRAD (*Ber.*, 1900, 33, 58—89. Compare Curtius and Lang, *Abstr.*, 1889, 369).—Several improvements in the preparation of ethyl aminoacetate hydrochloride are recommended. One is the careful granulating, while hot, of the mixture of glycocine hydrochloride and ammonium chloride and the subsequent drying of this in a large Victor Meyer bath at 115°.

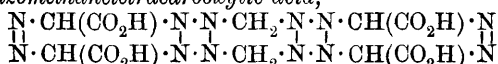
The compound obtained by Curtius and Lang from ethyl diazoacetate and described as tridiazooacetic acid is shown, by the aid of molecular weight determinations of the ethyl ester, to be *bisdiazooacetic acid*, $\text{CO}_2\text{H} \cdot \text{CH} \begin{array}{l} \text{N:N} \\ \text{N:N} \end{array} \text{CH} \cdot \text{CO}_2\text{H}$.

In its preparation, the impure sodium bisdiazooacetate is first washed with alcohol, then rubbed into a paste with water, and again treated in a similar manner until all carbonate is removed; if not thus purified,

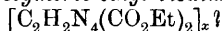
much hydrazine is formed on subsequent treatment with sulphuric acid. A 25 per cent. yield of the ethyl ester is obtained when the precipitated silver salt is washed with alcohol, ether, benzene, and then warmed with a benzene solution of slightly less than the theoretical amount of ethyl iodide; it melts at 113.5° and not at 110° . The silver salt exhibits characteristic colours with nitric acid which may be made use of in testing even impure bisdiazooacetic acid. The hydrates represented by Curtius and Lang as $C_3H_3N_6(CO_2H)_3 \cdot 3H_2O$ and $2H_2O$ are to be represented as $C_2H_2N_4(CO_2H)_2 \cdot 2H_2O$ and H_2O respectively. The statement that the hydrated salt, when heated at 100° , is easily converted into carbon dioxide and tetrazine cannot be substantiated. The anhydrous acid is obtained together with dihydrotetrazine when the hydrated acid is boiled with absolute alcohol; it forms a pale yellow powder melting at 180° , and is insoluble in ordinary solvents, but dissolves readily in alkalis; at 100° , it is slowly, but at its melting point rapidly, converted into carbon dioxide and dihydrotetrazine.

Dihydrotetrazinedicarboxylic acid, $CO_2H \cdot C \begin{smallmatrix} \text{NH} \cdot \text{N} \\ \text{N} \cdot \text{NH} \end{smallmatrix} > C \cdot CO_2H$, is formed when bisdiazooacetic acid is treated with potassium hydroxide, or as a bye-product in the conversion of ethyl diazoacetate into trisbisdiazomethanetetra-carboxylic acid; it forms long, colourless, glistening needles melting and decomposing at 287° , is sparingly soluble in water and even more sparingly in other solvents; the *potassium* salt crystallises in thick, colourless prisms and the *silver* salt forms a gelatinous precipitate.

Trisbisdiazomethanetetra-carboxylic acid,

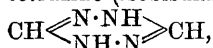


(Curtius and Lang's dicarboxylic acid), is obtained, together with the acid just described, by the action of potassium hydroxide on ethyl diazoacetate, but the separation is tedious; it forms long, colourless, hair-like needles which melt at 183° , and yield diazomethane. The *silver* salt, $3C_6H_8N_{12}(CO_2Ag)_4 \cdot 4AgNO_3$, forms a white powder, which, on treatment with ethyl iodide, yields a considerable amount of tarry matter together with a *polymeric ethyl bisdiazooacetate*,



which crystallises from alcohol in glistening plates melting at 232° . The compound obtained by Curtius and Lang on heating the acid, and stated to be $C_3H_6N_6$, is shown to have the formula $C_2H_4N_4$ and is 3:6-dihydro-1:2:4:5-tetrazine (*bisdiazomethane*), $CH_2 \begin{smallmatrix} \text{N} \cdot \text{N} \\ \text{N} \cdot \text{N} \end{smallmatrix} > CH_2$; its melting point, after recrystallisation from alcohol, is 149° , and after sublimation 154° ; Curtius and Lang gave 145° .

1:4-Dihydro-1:2:4:5-tetrazine (*isobisdiazomethane*),



Curtius and Lang's trimethintriazimide, may be obtained by the following methods: 1. By allowing bisdiazomethane to remain in contact with alcoholic potash for several weeks. 2. By heating dihydrotetrazinedicarboxylic acid with dilute hydrochloric acid. 3. By

heating bisdiazooacetic acid at its melting point. 4. By heating formylhydrazine at 150° (Ruhemann and Stapleton, *Trans.*, 1899, 75, 1131). It is, however, most readily obtained by heating crude bisdiazooacetic acid with absolute alcohol and a small amount of ethyl cinnamate; if the substances employed are not dry, a considerable amount of hydrazine formate is produced.

Dihydrotetrazine hydrochloride, $C_2H_4N_4HCl$, melting at 151° (compare Pellizzari, *Abstr.*, 1899, i, 859), platinichloride (Ruhemann and Stapleton, *loc. cit.*), *hydrobromide*, melting and decomposing at 136° , *hydriodide*, melting and decomposing at $134-135^{\circ}$, *oxalate*, $C_2H_4N_4H_2C_2O_4$, microscopic needles melting and decomposing at 164° , and an *acetyl* derivative, $CH \leq \begin{smallmatrix} N \cdot Ac \\ N \cdot NH \end{smallmatrix} N \cdot CH$, a syrup which slowly crystallises, have been prepared.

Sodium amalgam has no action on dihydrotetrazine; with tin and hydrochloric acid, it yields ammonium salts; with zinc dust and acetic acid, a small amount of methylhydrazine is obtained. When treated with benzoyl chloride by the Schotten-Baumann method, it is converted into *s*-dibenzoylhydrazine melting at 238° ; Curtius (*Abstr.*, 1891, i, 56) and Struve (*ibid.*, 1895, i, 35) give 233° , and Borrisow (*Zeit. physiol. Chem.*, 1894, 19, 505) 237° .

Most oxidising agents either do not attack dihydrotetrazine or else completely destroy it; when, however, nitrous anhydride is led into an aqueous solution of the tetrazine at 0° , and, after some time, the solution evaporated, colourless crystals of 1:2:4-triazole nitrate, $NH \leq \begin{smallmatrix} CH:N \\ CH:N \end{smallmatrix} HNO_3$, are formed; this separates from alcohol in octa-

hedral twinned crystals or in needles melting at 138° , and sublimes when carefully heated; it yields the following double salts:

$3(C_2H_3N_3, HNO_3) \cdot 4AgNO_3$, white precipitate; $C_2H_3N_3, HNO_3, 2HgCl_2$, large, octahedral-shaped crystals; $C_2H_3N_3, NaNO_3$, small, colourless needles; $C_2H_3N_3, AgNO_3$ or $C_2H_2AgN_3, HNO_3$, heavy precipitate; $C_2H_2(CuNO_3)N_3$, blue precipitate.

Free triazole cannot be obtained by the action of alkalis on the nitrate; it is best formed by treating the hydrochloride with silver oxide. The product thus formed is identical with that obtained by Freund and Meineke (*Abstr.*, 1897, i, 113). The *hydrochloride* is obtained when the nitrate is heated with concentrated hydrochloric acid at 150° , or better, by reducing the nitrate with sodium amalgam and alcohol, and then treating with alcoholic hydrogen chloride. It forms colourless, rhombic plates melting at $168-169^{\circ}$, and is readily soluble in water.

J. J. S.

Diazocaffeine. By MOSES GOMBERG (*Amer. Chem. J.*, 1900, 23, 51-69).—When aminocaffeine, dissolved in strong hydrochloric acid, is treated with a solution of sodium nitrite at -10° , a solution is obtained which exhibits all the reactions of a diazo-compound; it stains the skin a dark red, quickly changing to brown, and on raising the temperature of the liquid, a gas, probably nitrogen, is evolved, and a small quantity of a very bulky, amorphous compound separates

Diazocaffeine also appears to be produced by the action of nitric acid on aminocaffeine in the cold.

Caffeine-p-azophenol, $C_8H_9O_2N_4 \cdot N_2 \cdot C_6H_4 \cdot OH$, formed on mixing solutions of diazocaffeine hydrochloride and phenol, crystallises from acetic acid in red needles insoluble in cold water.

Caffeine-p-azodimethylaniline, $C_8H_9O_2N_4 \cdot N_2 \cdot C_6H_4 \cdot NMe_2$, separates from boiling chloroform on addition of ether in long, dark red needles, having a beautiful, greenish iridescence, and on pouring the hot solution in chloroform into boiling toluene is precipitated in the form of dark, steel-blue needles. It is scarcely soluble in water, sparingly soluble in alcohol, benzene, or dilute acetic acid. The *hydrochloride* is fairly stable when dry, but easily decomposed by water. On reduction with stannous chloride, the substance yields dimethylaniline and aminocaffeine.

Caffeineazo-2:4-diaminobenzene, $C_8H_9O_2N_4 \cdot N_2 \cdot C_6H_3(NH_2)_2$, is brown, dissolves sparingly in the usual media, and does not melt at 285° .

Caffeineazo- β -naphthol, $C_8H_9O_2N_4 \cdot N_2 \cdot C_{10}H_6 \cdot OH$, separates from glacial acetic acid in minute, ponceau-red needles, and is soluble in hot benzene and chloroform.

When diazocaffeine is allowed to react with acetoacetic acid, an *azo-compound*, $COMe \cdot C(N_2 \cdot C_8H_9O_2N_4)_2 \cdot CO_2H$, is produced, which crystallises in dark blue crystals with a green reflex, and is sparingly soluble in alcohol or benzene, but fairly soluble in water or chloroform. It shows signs of fusion at 200° , but is not melted at 285° .

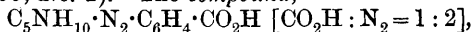
With propylacetoacetic acid, diazocaffeine affords a dark brown, crystalline *substance*, $CPr^a(N_2 \cdot C_8H_9O_2N_4)_2 \cdot CO_2H$, which has a bluish tint, but no metallic lustre, and is sparingly soluble in water; it does not melt at 285° .

The *compound*, $C_7H_7 \cdot C(N_2 \cdot C_8H_9O_2N_4)_2 \cdot CO_2H$, obtained with benzylacetoacetic acid, forms dull black crystals from a mixture of chloroform and ether, and does not melt at 285° .

Diazocaffeine acts on an alkaline solution of nitroethane, forming a *substance*, $NO_2 \cdot CMe(N_2 \cdot C_8H_9O_2N_4)_2$, which separates from a mixture of chloroform and ether in deep blue flakes melting at $218-219^\circ$.

With nitropropane and diazocaffeine, a similar *compound* is obtained, which forms very light, deep blue flakes, having a slight metallic lustre and melting with decomposition at $237-238^\circ$. A. L.

Mixed Diazoamino-compounds. By OTTO WALLACH and A. TEWES (*Chem. Centr.*, 1899, ii, 1050—1051; from *Nachr. k. Ges. Wiss. Göttingen*, 1899, No. 2).—The *compound*,



prepared by the action of piperidine on diazotised *o*-aminobenzoic acid, crystallises in white leaflets, melts at 84° , and forms an ammonium salt which is insoluble in ether, and a silver salt which crystallises in colourless needles. The isomeric *meta*-compound, prepared similarly from diazotised *m*-aminobenzoic acid, melts at 123° and the *para*-compound melts and decomposes at 158° . By the action of diazotised *p*-aminophenol on piperidine, the *compound*, $C_5NH_{10} \cdot N_2 \cdot C_6H_4 \cdot OH$ [$OH : N_2 = 1 : 4$], is formed; it melts at $87-88^\circ$. The corresponding *com-*

pound, $C_5NH_{10} \cdot N_2 \cdot C_6H_4 \cdot OMe$, similarly prepared from anisidine, crystallises in large, yellow crystals, and melts at $33-34^\circ$. The reactions of the preceding compounds resemble those of benzene-diazopiperidide. By the action of bromine, dissolved in carbon disulphide, on benzene-diazopiperidide, the *hydrobromide*, $C_5NH_{10} \cdot N_2 \cdot Ph \cdot HBr$, is precipitated, whilst the *bromide*, $C_5NH_{10} \cdot N_2 \cdot C_6H_4 \cdot Br$ [$Br : N_2 = 1 : 4$], remains in solution. The former compound, when warmed with dilute sulphuric acid, yields phenol, together with a considerable amount of tribromophenol, which melts at 92° . The bromide crystallises in yellow leaflets, melts at 55° , and is decomposed by warming with concentrated hydrobromic acid, forming *p*-dibromobenzene. The *bromide*,

$C_5NH_{10} \cdot N_2 \cdot C_6H_3MeBr$ [$Me : Br : N_2 = 1 : 3 : 4$], obtained by the action of bromine on *p*-toluenediazopiperidide, forms yellow crystals, melts at $52-53^\circ$, and when boiled with concentrated hydrobromic acid yields 3 : 4-dibromotoluene.

When the sodium salt of diazobenzenepiperididesulphonic acid,

$C_5NH_{10} \cdot N_2 \cdot C_6H_4 \cdot SO_3Na$ [$SO_3Na : N_2 = 1 : 4$], is treated with bromine in the cold, dibromodiazobenzeneperbromide, $C_6H_3Br_2 \cdot NBr \cdot NBr_2$ [$N_2 : Br_2 = 1 : 3 : 4$], is formed. When the perbromide is boiled with alcohol, it yields 1 : 2 : 4-tribromobenzene, and by the action of ammonia it forms diazobenzeneimide. The imide melts at 62° , is volatile in steam, and when boiled with concentrated hydrobromic acid forms 2 : 4 : 6-tribromoaniline.

In the conversion of diazobenzenepiperididesulphonic acid into dibromodiazobenzene perbromide, the replacement of the sulphonic group by bromine in ice-cold solutions is remarkable. E. W. W.

Nitrogen which can be split off from Proteids by Acids. By YANDELL HENDERSON (*Zeit. physiol. Chem.*, 1900, 29, 47—50).—Hausmann has stated (Abstr., 1899, i, 653) that the amount of nitrogen obtainable in various forms by decomposing proteid with acids is characteristic for different proteids. This is not so; with either hydrochloric or sulphuric acid, the amount of nitrogen is most variable, depending on the concentration of the acid and the duration of the action.

W. D. H.

Nitrogen in Primary Albumoses. By ERNST FRIEDMANN (*Zeit. physiol. Chem.*, 1900, 29, 51—58).—The nitrogen obtained from primary albumoses (proto- and hetero-albumose) was estimated as loosely bound nitrogen, basic nitrogen, and acid nitrogen by Hausmann's method. The two proteids gave different results. The results are different from those previously given by Pick and by Hausmann, and if the criticism of the method contained in the preceding abstract is upheld, this is easily accounted for.

W. D. H.

Physical alterations in Proteids. By W. PAULI (*Pflüger's Archiv*, 1899, 78, 315—345).—The investigation was undertaken with the view of elucidating the colloidal condition of proteids, the special point selected being the coagulation temperature and its variations when different amounts of various neutral salts are added to the solution. Thus a gradual increase in the percentage of various chlorides raises the coagulation temperature up to a certain point, when it begins to fall again; this is most marked with the chlorides

of lithium, magnesium, and barium; the alteration of the coagulating point is not absolutely proportional to the amount of salt added. Similar results were obtained with the bromides; iodides, on the other hand, depress the coagulation temperature. Various other groups of salts, nitrates, sulphates, acetates, &c., were also investigated, and the results of different salts of the same metal compared. The influence of pairs of salts on coagulation temperature was also examined. The results, as well as the effect of precipitation of globulin by neutral salts, are believed to be due to the entrance of ions into the proteid molecule.

W. D. H.

Oxidation of Crystalline Egg-albumin by Hydrogen Peroxide. By FRIEDRICH W. SCHULZ (*Zeit. physiol. Chem.*, 1900, 29, 86—104).—By the action of hydrogen peroxide on crystallised egg-albumin, a new substance, *oxyprotein*, with the general characters of oxyprotosulphonic acid, is obtained; this is an oxidation product, not a decomposition product of albumin. There is, however, a difference between the two substances mentioned; the sulphur of the proteid which can be removed by alkali is not oxidised, but is so much diminished that more delicate methods have to be adopted for its detection. The hydrolysing action of hydrogen peroxide is ascribed to the fact that this reagent strengthens the hydrolysing action of acid and alkalis. The crystalline proteid used in these experiments was prepared by the acid method; it differs from the crystalline egg-albumin prepared by Hofmeister's method in elementary composition, and is probably in a hydrated condition.

W. D. H.

Crystallised Fibrin. By LOUIS MAILLARD (*Compt. rend.*, 1900, 130, 192—194. Compare Abstr., 1899, i, 466, and ii, 777).—Prolonged treatment of the granular deposit from antidiphtheric serum with boiling alcohol and 5 per cent. hydrochloric acid destroys the crystallised fibrin, but even after 6 hours digestion with the acid, small granules of a crystalline substance remain. An examination of the product by the aid of the polarising microscope and micro-chemical reactions indicates the presence of a proteid substance in different stages of crystallogenesis; some of the granules obtained from serum after four years exhibit a distinctly crystalline character when viewed in polarised light. The deposit, before treatment with hydrochloric acid, also contains spherical aggregates of doubly refracting needles, having the properties of calcium palmitate.

G. T. M.

The Proteids of Cows' Milk. By KARL STORCH (*Monatsh.*, 1899, 20, 837—846).—Full directions are now given for the purification of the substances *a* and *b* previously described (compare Abstr., 1897, ii, 420). Substance *a* is a nucleo-albumin, characterised by its composition, acid reaction, insolubility in water and concentrated solutions of sodium sulphate, magnesium sulphate, or sodium chloride, also by its solubility in small quantities of alkali, sodium carbonate, or lime-water, to solutions of neutral reaction, and by remaining uncoagulated when such solutions are boiled.

Substance *b* is a nucleo-histon, and is characterised by its composition and behaviour towards water, acids, alkalis, and neutral salts, especially by the fact that 0·8 per cent. hydrochloric acid decomposes it into a soluble and an insoluble portion; the former may be precipitated by alcohol or ammonia in excess, and has the properties of a histon; the latter has those of a nuclein. Other properties of *a* and *b* are minutely tabulated. The average percentage composition is as follows, Hammarsten's analysis of casein being added for comparison:

	C.	H.	N.	S.	P.	O.
Substance <i>a</i>	54·43	6·805	14·815	0·635	0·79	22·525
Substance <i>b</i>	49·125	5·91	14·13	1·585	2·085	27·135
Casein (Hammarsten)	53·0	7·0	15·7	0·8	0·85	22·65

R. L. J.

Formation of Methæmoglobin. By GUSTAV HÜFNER (*Chem. Centr.*, 1899, ii, 484; from *Arch. Anat. Phys.*, 1899, 491—499. Compare von Zeynek, this vol., i, 196).—Hoppe-Seyler's theory of the formation of methæmoglobin from oxyhæmoglobin by elimination of only a portion of the oxygen is not correct, for in the action of potassium ferricyanide on oxyhæmoglobin, not one but two atoms of oxygen are set free. Hydroxylamine hydrochloride also causes a rapid conversion of oxyhæmoglobin into methæmoglobin, but hydrazine hydrate only reduces oxyhæmoglobin to hæmoglobin, which is then decomposed by excess of the hydrate forming hæmochromogen. Since albumin and the colouring matter containing iron are formed by the reducing action of hydrazine hydrate, probably both these atomic complexes are contained in hæmoglobin, and are combined in the molecule by means of oxygen.

E. W. W.

Nucleic Acid from Salmon Milt. By OSWALD SCHMIEDEBERG (*Chem. Centr.*, 1899, ii, 721—722; from *Arch. exp. Path. Pharm.*, 43, 57—83).—Pure nucleic acid was prepared from the material left by Miescher, which also contained protamine, by means of the copper-alkali method, which depends on the solubility of the copper compounds of proteid substances, and the insolubility of other copper compounds in a solution of alkali hydroxide in alcohol. From the analysis of the copper compound, the formula of nucleic acid was calculated to be $C_{40}H_{56}O_{16}N_{14}, 2P_2O_5$. By the decomposition of nucleic acid, the bases adenine and guanine are formed, and theoretically a residue of $C_{30}H_{46}O_{15}N_4, 2P_2O_5$, or nucleotinphosphoric acid, should be left, but attempts to isolate this compound failed. From the solution, obtained by warming copper nucleate with adenine and guanine in dilute potassium hydroxide solution for 10—15 minutes at 40—45° and then cooling and acidifying with acetic acid, cupric chloride precipitates a substance which contains more purine bases than the original nucleic acid, but having properties very similar to this acid. Since in this case the precipitate cannot contain the bases combined in the form of esters, they are also probably combined in nucleic acid, as salts rather than as esters. The hypothetical nucleotinphosphoric acid has probably an ester-like constitution, for it is decomposed by heating with dilute hydrochloric acid, one half of the

base being more easily removed than the other, which requires a 10—20 per cent. solution of acid. Melanins containing phosphorus are formed by heating nucleic acid with hydrochloric acid.

E. W. W.

Co-existence of a Reducing Enzyme and an Oxidising Enzyme in the Animal Organism. By J. ABELOUS and ERNEST GÉRARD (*Compt. rend.*, 1899, 129, 1023—1025. Compare Abstr., 1899 ii, 681).—In a former communication, the authors showed that the amount of nitrite found in the liquid resulting from the action of an aqueous extract of the kidney of the horse on a nitrate decreased after the action had been going on for about 24 hours. This diminution of nitrite they now prove to be due to its oxidation by an oxidising enzyme (oxydase), which is present in the renal extract. By digesting the extract with papain or trypsin, its reducing action is almost entirely destroyed, so that the oxidising action alone goes on. Conversely, by conducting the experiment in an atmosphere of inert gas, like hydrogen, the oxidising enzyme is powerless, and the reducing enzyme alone acts.

H. R. LE S.

Enzymes. By N. SACHAROFF (*Chem. Centr.*, 1899, ii, 723 ; from *Centr. Bakt. Parasit.*, [i], 26, 189—194. Compare *ibid.*, 24, Nos. 18—19, and Abstr., 1899, ii, 786).—Photographs showing the effect of antiseptics on the power of papain of dissolving gelatin are reproduced in the original paper. From these photographs, it is evident that this power depends on the presence of a substance, iron nuclein or bionuclein, which possesses both oxidising and reducing properties. When the bionuclein is separated from the enzyme by the action of hydrogen peroxide, it loses its dissolving power, but this may be restored by adding a very small quantity of the active enzyme or of active bionuclein.

The formation of oxyglutin, the insoluble product of the action of papain on gelatin, is also shown by means of photographs. In the formation of oxyglutin, more oxygen is required than is necessary for the solution of the gelatin. The soluble gelatin is formed by the action of the enzyme as an intermediate product in the production of oxyglutin.

The gelatin dissolved in neutral solutions is to be distinguished from that which is formed in alkaline or acid liquids by the action of dilute papain solution.

E. W. W.

Organic Chemistry.

Action of Amalgamated Aluminium on Alcohols. Aluminium Alkyloxides. By WETSCHIASLAW E. TISTSCHENKO (*J. Russ. Phys. Chem. Soc.*, 1899, 31, 694—770; 784—872. Compare Abstr., 1899, i, 408).—A number of aluminium alkyloxides have been prepared by the action of amalgamated aluminium on the corresponding alcohols. With absolute ethyl alcohol, the action is very slow in the cold, but quicker at 100°; the observation of Wislicenus and Kaufmann (Abstr., 1895, i, 437), that the action only occurs if traces of water are present, is hence inaccurate, as also is the statement of Konowaloff (*Pharm. Zeit. Russ.*, 1896, 35, 328), that amalgamated aluminium does not act on alcohol containing a small quantity of water, even on boiling.

Aluminium methoxide is a light grey powder, has a sp. gr. of 1.35, and, on heating, decomposes with evolution of gases which burn with a luminous flame. The ethoxide is a grey powder melting at 134—135° and boiling at 205° under 14 mm. pressure; it has a sp. gr. 1.1423 at 20°/0° and 1.1545 at 0°/0°. Aluminium propoxide melts at 106—107°, boils at 250.5° under 16 mm. pressure, and has a sp. gr. 1.0578 at 20°/0° and 1.0650 at 0°/0°. The isobutoxide forms acicular crystals which melt at 212—214° and dissolve in benzene, ether, or isobutyl alcohol; it boils at 239° under 4 mm. pressure, and has a sp. gr. 0.9749 at 20°/0°. Aluminium *n*-butoxide crystallises in needles melting at 101.5—102°, and boiling at 284.5° under 10 mm. pressure; it has a sp. gr. 1.0251 at 20°/0°, and is soluble in the corresponding alcohol, and also in ether, benzene, or toluene. The isoamyloxide melts at 225—230°, and boils at 282° under 4 mm. pressure; it is soluble in benzene, ether, toluene, or isoamyl alcohol, and has a sp. gr. 1.0021 at 20°/0°, and 1.0117 at 0°/0°. The isopropoxide, which crystallises in octahedra of the tetragonal system, melts at 118—118.5°, boils at 136.5° under 6 mm., and at 153—155° under 15.5 mm. pressure; it has a sp. gr. 1.0346 at 20°/0°, and 1.0533 at 0°/0°. Aluminium secondary butoxide is a thick, transparent liquid boiling at 181—181.5° under 8 mm. pressure, and having a sp. gr. 0.9671 at 20°/0°; its index of refraction for sodium light at 20° is 1.44428. From methylpropylcarbinol, aluminium secondary amyloxide is obtained as a mobile liquid, solidifying to a glassy mass when cooled in a mixture of ether and solid carbon dioxide; it boils at about 210—212° under 8 mm. pressure. Trimethylcarbinol yields aluminium tertiary butoxide, which crystallises from benzene in beautiful, thick, rhombohedral plates belonging to the triclinic system: [$\alpha=105^\circ$, $\beta=117^\circ$, $\gamma=100^\circ 20'$]; it melts at 206.5—207°, but does not distil undecomposed. Aluminium tertiary amyloxide (from dimethylethylcarbinol) melts at 199—200°, and is soluble in benzene or toluene, separating from the latter in needles or thin plates.

By measuring the quantities of hydrogen evolved in equal times during the reactions between amalgamated aluminium and various alcohols, it is found that the speed of reaction falls as the molecular weight of the alcohol increases, and that, in the case of isomeric alcohols, the speed is greater for the primary, than for the secondary, alcohol.

Amalgamated aluminium acts on ethyl acetoacetate, giving the ethyl aluminooacetoacetate obtained by Conrad by the interaction of potassium aluminate and ethyl acetoacetate (Abstr., 1878, 26). *Ethyl aluminomalonate*, $\text{Al}[\text{CH}(\text{CO}_2\text{Et})_2]_3$, obtained along with carbon dioxide, saturated and unsaturated hydrocarbons, ethyl acetate and alcohol, when ethyl malonate and amalgamated aluminium interact, crystallises from benzene in long, lustrous needles melting at $94-95^\circ$.

The aluminium derivatives of isobutyl and isoamyl alcohols, and of ethyl acetoacetate and malonate, have molecular weights in freezing benzene corresponding with those required for the formula $\text{Al}(\text{OR})_3$.

The differences between the boiling points (at the same pressure) of two consecutive members of the homologous series of aluminium alkyl oxides vary from 41° to 43° , and the secondary alcohol derivatives have boiling points approximately 100° lower than those of the isomeric primary compounds.

Water acts on the aluminium alkyl oxides, converting them into aluminium hydroxide and the corresponding alcohol. On warming aluminium alkyl oxides derived from primary alcohols with other primary alcohols, replacement of the alkyl radicle with the higher molecular weight takes place more easily than the inverse reaction; and, if the alcohols are isomeric, the primary replaces the secondary, and the latter replace the tertiary from combination with aluminium. This reaction may be used in the preparation of aluminium alkyl oxides not otherwise obtainable; for example, *aluminium allyloxide*, $\text{Al}(\text{OC}_3\text{H}_5)_3$, is obtained by the interaction of allyl alcohol and the aluminium derivative of dimethylethylcarbinol in benzene solution; it is a white powder which melts and decomposes at about 150° , and dissolves slightly in allyl alcohol or benzene. It has a sp. gr. 1.1861 at $20^\circ/0^\circ$. This compound is the first aluminium derivative of an unsaturated alcohol which has been prepared.

Hydrochloric acid acts on aluminium isopropoxide or isobutoxide, yielding a compound of the corresponding alcohol with aluminium chloride— $\text{AlCl}_3 \cdot 3\text{C}_3\text{H}_7 \cdot \text{OH}$ or $\text{AlCl}_3 \cdot 3\text{C}_4\text{H}_9 \cdot \text{OH}$; these compounds are hygroscopic and are decomposed by water. On ethyl or isopropyl iodide, ethylene bromide, or chloroform, the aluminium alkoxides have no action.

[With A. GABOUNIA.]—On heating aluminium isopropoxide with β -dibromopropyl alcohol, *aluminium β -dibromopropoxide*, $(\text{CH}_2\text{Br} \cdot \text{CHBr} \cdot \text{CH}_2 \cdot \text{O})_3\text{Al}$, is obtained as a colourless, porous mass, which, on keeping, assumes a reddish tint.

[With M. G. KISSELEFF.]—Acetic anhydride acts on aluminium ethoxide, giving ethyl acetate and aluminium acetate. The latter, hitherto only known in solution, is a light, white powder smelling of acetic acid, owing to decomposition by the moisture of the air. It

dissolves in cold water, and the solution may be boiled without decomposing. With aluminium ethoxide, carbon dioxide forms aluminium diethoxyethylcarbonate, $\text{Al}(\text{OEt})_2 \cdot \text{CO}_2\text{Et}$. Sulphur dioxide yields an analogous compound of the composition $\text{OEt} \cdot \text{Al}(\text{SO}_3\text{Et})_2$.

When subjected to dry distillation, the aluminium alkylloxides, as a rule, decompose, yielding the corresponding ether, alcohol, and ethylene hydrocarbon, small quantities of aldehydes, hydrogen, and paraffinoid hydrocarbons being also obtained.

[With N. N. PUSHIN.]—Aluminium methoxide, when heated, is first resolved into alumina and dimethyl ether, the latter partially decomposing at higher temperatures with the formation of methane, carbon monoxide, and hydrogen in about equal volumes. In the case of the aluminium derivative of trimethylcarbinol, the pure alcohol is obtained without any admixture of the corresponding ether. These results are, on the whole, concordant with those obtained by Gladstone and Tribe (*Trans.*, 1882, 41, 5).

Dimethyl ether, when heated, splits up first into methane and formaldehyde, the latter at higher temperatures being resolved into equal volumes of hydrogen and carbonic oxide.

[With N. MARAZOUEFF.]—Methyl ethyl and methyl propyl ethers, when heated, suffer decomposition, with formation of carbon monoxide, hydrogen, and hydrocarbons of the ethylene series. Other ethers give similar results. T. H. P.

Rancidity of Fats. By ISKAR NAGEL (*Amer. Chem. J.*, 1900, 23, 173—176).—In refining rancid fats or oils, the free fatty and unsaturated acids are removed as sodium salts by means of an aqueous solution of sodium silicate; the non-volatile lactones are removed, after this treatment, by converting them into salts of hydroxy-fatty acids by boiling for several hours with a small quantity of aqueous sodium carbonate or hydroxide. Non-volatile aldehydes are eliminated by warming with aqueous sodium hydrogen sulphite, whilst the non-volatile acetals are removed by heating the oil with dilute sulphuric acid. Alcohols, esters of fatty and hydroxy-acids, volatile aldehydes, acetals, and terpenes are removed finally by steam distillation.

W. A. D.

Japan Wax. By ADOLF C. GEITEL and G. VAN DER WANT (*J. pr. Chem.*, 1900, [ii], 61, 151—156. Compare Eberhardt, *Inaug. Diss.*, *Strassburg*, 1888).—Two samples of the wax gave, on hydrolysis, soluble acids, 5.96 and 4.66; insoluble acids, 90.62 and 90.66; total acids, 96.58 and 95.92 respectively. The soluble acids were of fatty consistency, only soluble in a large bulk of water, and gave soluble alkali-salts, but sparingly soluble barium and calcium salts; the green copper salt, on analysis, gave numbers corresponding with the formula, $\text{C}_3\text{H}_{12}\text{O}_4\text{Cu}$, for copper suberate, whilst the titration of the acid gave a mean molecular weight of 162; it is suggested that oxidised substances are produced in the bleaching of the wax, which, on hydrolysis, break down into heptaldehyde and lower fatty acids. Pure glycerol was isolated from the aqueous liquors.

The insoluble acids contain a little oleic acid, but consist mainly of palmitic acid, together with a dibasic *japanic acid*, $\text{C}_{20}\text{H}_{40}(\text{CO}_2\text{H})_2$.

This can readily be separated from the palmitic acid by adding alcoholic potash to a 10 per cent. alcoholic solution of the fatty acids, draining the less soluble potassium salt at about 60° and crystallising the acid from alcohol or chloroform. In this way, the acid is obtained in minute, white flakes and melts at 117·7—117·9°. It only absorbs a trace of iodine and is therefore saturated, and contains no hydroxyl group. A molecular weight determination in boiling alcoholic solution gave $M = 364$ and 365 , whilst titration gave $M = 186·2 \times n$. When heated at 150°, the acid begins to lose water with partial formation of an anhydride, but when heated at 200°, it also loses carbon dioxide and gives a suberone-like ketone, $C_{20}H_{40} \cdot CO$; this was separated by extracting with alcoholic potash and crystallising from alcohol, when it was obtained in minute needles melting at 82—83°.

The acid probably exists in the wax as a mixed *glyceride* containing 1 mol. palmitic acid and 1 mol. janicic acid; by extracting the fatty acids with alcohol, separating the tripalmitin by crystallising from benzene, and extracting repeatedly with absolute alcohol, a hard mass was obtained which melted at 43—45° and had an ether number 252·6, the theory for the glyceride being 253·4. T. M. L.

Substituted Dibasic Acids. Conversion of an Acid Chloride into an Anhydride by the Action of Haloid Acids. By ALB. J. J. VANDEVELDE (*Chem. Centr.*, 1900, i, 404; from *Bull. Acad. roy. Belg.*, [iii], 37, 680—700. Compare *Bull. Acad. roy. Belg.*, [iii], 29, 609).—By the action of bromine and iron on succinic chloride,

dibromomaleic anhydride, $\begin{array}{c} \text{CBr} \cdot \text{CO} \\ || \\ \text{CBr} \cdot \text{CO} \end{array} > \text{O}$, is formed; it melts at 112°

and boils at 225°. Barium dibromomaleate, $C_2Br_2O_4Ba$, crystallises from water, in which it is easily soluble, in lustrous needles, and is precipitated from its aqueous solution by alcohol. Acetic chloride is completely charred by the action of bromine and iron, and dibromomaleic acid is not formed. Citraconic and mesaconic acids, under similar conditions, yield bromocitraconic anhydride, $\begin{array}{c} \text{CMe} \cdot \text{CO} \\ || \\ \text{CBr} \cdot \text{CO} \end{array} > \text{O}$,

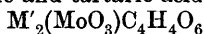
melting at 98°. By the prolonged action of chlorine and iron on chlorofumaric chloride, dichloromaleic anhydride and dichloromaleic chloride, $\text{COCl} \cdot \text{CCl} : \text{CCl} \cdot \text{COCl}$, are obtained. The former melts at 119°. The latter, which may also be prepared by the action of phosphorus pentachloride on dichloromaleic anhydride, forms an oil, has a pungent odour, boils at 192—194°, is volatile in steam, and is soluble in organic solvents. Unlike other acid chlorides, it does not fume in the air, and is not decomposed by boiling with water or alkali. It is attacked, however, by alcoholic potassium hydroxide solution.

E. W. W.

Some Complex Salts of Tartaric and Malic Acids, and their Specific Rotatory Power. II. By ARTHUR ROSENHEIM and HERMANN ITZIG (*Ber.*, 1900, 33, 707—718. Compare this vol., i, 135).—Boiling concentrated aqueous solutions of normal alkali tartrates dissolve precipitated tungstic acid to form soluble, amorphous "tungstotartrates" of the type $M'_2(WO_3)_4C_4H_4O_6$; the

potassium double salt (with $5\text{H}_2\text{O}$) in concentrated solutions (more than 3 grams per 100 c.c.) has $[\alpha]_D + 340^\circ$ at 11° ; the *sodium* salt (with $2\text{H}_2\text{O}$) has $[\alpha]_D + 273^\circ$ at 17° ; and the *ammonium* salt (with $1\text{H}_2\text{O}$), $[\alpha]_D + 296^\circ$ at 12° (compare Landolt's *Optische Drehungsvermögen*, 2nd ed., 220). In dilute solutions, these double salts, unlike the complex beryllium tartrates formerly described (*loc. cit.*), undergo hydrolysis, the specific rotatory power diminishing very greatly; the high rotation in concentrated solution is probably due to the complex $\text{CO}_2\text{M}'\cdot[\text{CH}\cdot\text{OH}]_2\cdot\text{CO}_2\cdot\text{WO}_2\cdot\text{OM}'$. Sodium metatungstate does not increase the specific rotatory power of tartaric acid, but sodium paratungstate has a greater effect than the ordinary tungstate, a maximum value of $[\alpha]_D + 364.5^\circ$ at 14° being reached when the substances are in the ratio $1\text{C}_4\text{H}_6\text{O}_6 : \frac{1}{5}\text{Na}_{10}\text{W}_{12}\text{O}_{41}$.

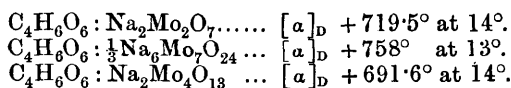
Double salts of molybdic and tartaric acids of the type



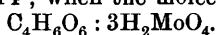
could not be obtained by the interaction of alkali tartrates and molybdic acid, but were prepared by evaporating solutions containing a mixture of the alkali bimolybdate, $\text{M}'_2\text{Mo}_2\text{O}_7$, and the alkali hydrogen tartrate; the specific rotatory power of the *potassium* salt (with $4\text{H}_2\text{O}$), and the *sodium*, *lithium*, and *magnesium* double salts (each with $5\text{H}_2\text{O}$), is given in the following table. This also shows the molecular ratio of tartaric acid, and the metallic molybdate in the double salts, and indicates errors formerly made by Gernez (compare *Opt. Drehungsvermögen*, *loc. cit.*) with regard to these ratios.

Molecular ratio.		Maximum $[\alpha]_D$.	
Gernez.	Authors.	Gernez.	Authors.
—	$1\text{K}_2\text{MoO}_4 : 1\text{C}_4\text{H}_6\text{O}_6$	—	$+ 550.7^\circ$ at 15°
$1\text{Na}_2\text{MoO}_4 : 1\text{C}_4\text{H}_6\text{O}_6$	$1\text{Na}_2\text{MoO}_4 : 1\text{C}_4\text{H}_6\text{O}_6$	$+ 517^\circ$ at 17°	$+ 543.6^\circ$ at 17° ($c = 10.286$)
$2\text{Li}_2\text{MoO}_4 : 1\text{C}_4\text{H}_6\text{O}_6$	$1\text{Li}_2\text{MoO}_4 : 1\text{C}_4\text{H}_6\text{O}_6$	$+ 484^\circ$ at 16°	$+ 489.3^\circ$ at 16°
$2\text{MgMoO}_4 : 1\text{C}_4\text{H}_6\text{O}_6$	$1\text{MgMoO}_4 : 1\text{C}_4\text{H}_6\text{O}_6$	$+ 523^\circ$ at 16°	$+ 521^\circ$ at 20°
$\frac{2}{3}(\text{NH}_4)_6\text{Mo}_7\text{O}_{24} : 1\text{C}_4\text{H}_6\text{O}_6$	$\frac{1}{3}(\text{NH}_4)_6\text{Mo}_7\text{O}_{24} : 1\text{C}_4\text{H}_6\text{O}_6$	$+ 781^\circ$ at 17°	$+ 790^\circ$ at 14°

All the salts are strongly hydrolysed in dilute solution, so that the specific rotatory power rapidly falls on diluting the concentrated solutions; the rotatory power, however, increases in an extraordinary degree on raising the temperature. The maximum rotatory power of solutions containing tartaric acid and sodium bimolybdate, paramolybdate, and tetramolybdate respectively, corresponds with the following ratios:



The sodium molybdotartrate, $\text{MoO}_2(\text{NaC}_4\text{H}_4\text{O}_6)_2$, obtained in solution by the interaction of sodium hydrogen tartrate and molybdic acid (Henderson and Barr, *Trans.*, 1896, 69, 1451), has $[\alpha]_D 252.3^\circ$ at 12° , which is not changed on diluting. Mixtures of molybdic acid and tartaric acid in solution gave maximum values $[\alpha]_D + 506^\circ$ at 17° , and $[\alpha]_D + 498^\circ$ at 14° , when the molecular ratio was



W. A. D.

Formation of Crystalline Manganese Oxalate by the Oxidation of Citric Acid with Potassium Permanganate. By GEORGES DENIGÈS (*J. Pharm.*, 1900, [vi], 11, 102—104. Compare this vol., i, 89).—When citric acid is oxidised with potassium permanganate, the oxalic acid found amongst the oxidation products gradually separates out as crystalline manganese oxalate. Some of the crystals are prismatic and of a rose colour, and correspond with the formula $\text{MnC}_2\text{O}_4 + 3\text{H}_2\text{O}$; the others are white, hexagonal crystals, and contain only $2\text{H}_2\text{O}$.

Crystalline manganese oxalate may also be obtained by the slow double decomposition of a mixture of manganese sulphate and ammonium oxalate, acidified with dilute acetic acid. If the decomposition is effected in the cold, the rose crystals are obtained, whereas, in boiling solution, the white, hexagonal crystals are formed.

H. R. LE S.

Melting Point of Chloral Hydrate. By C. G. L. WOLF (*J. Physical Chem.*, 1900, 4, 21—32).—The author has examined the phenomena of fusion of chloral hydrate, and considers that the variations observed in the melting point are not due to the existence of two modifications, but to dissociation, and that only one form of the compound exists in the melted mass, both the forms obtained by Pope (*Trans.*, 1899, 75, 455) giving similar results. The temperature at which the undissociated compound, the dissociation products, and the liquid are in equilibrium is about 47° , but the melting point for the undissociated compound itself is above 72° , at which temperature its vapour pressure is about 22 mm.

L. M. J.

Molecular Weight of the Aldols. By LEOPOLD KOHN (*Monatsh.*, 1900, 21, 80—97).—The molecular weights of various aldols and their polymerisation products have been determined by the method of Bleier and Kohn (this vol., ii, 192). It is found that "for each aldol there is a temperature above which only a unimolecular type can exist and below which two different molecular forms can exist, namely, a bimolecular form, which is unstable, and a unimolecular form; the temperature at which the depolymerisation of the double molecule takes place lies near to the boiling point of the aldol under a low pressure."

The various theoretical considerations do not lend themselves to abstraction.

R. H. P.

Mesityl Oxide. By HERMANN PAULY and HANS LIECK (*Ber.*, 1900, 33, 500—504).—*Bromomesityl oxide*, $\text{C}_6\text{H}_3\text{Br}\cdot\text{CMe}_2$, obtained by the action of alcoholic potash (1 mol.) on an alcoholic solution of mesityl oxide dibromide (Claisen, this Journ., 1876, i, 985) and subsequent precipitation with water, distils at $60\text{--}61^\circ$ under 20 mm. pressure, and has a sp. gr. 1.2832 at $11^\circ/4^\circ$; it has an extremely irritating action on the mucous membrane, and readily reduces Fehling's solution and silver oxide. Its *dibromide* crystallises in needles melting at 143° . *Mesityl oxide dichloride*, $\text{CHClAc}\cdot\text{CClMe}_2$, obtained by saturating an ethereal or alcoholic solution of mesityl oxide with chlorine at low temperatures, is a colourless liquid distilling at 77° under 12 mm.

pressure and having a sp. gr. 1.1942 at 11°/4°. *Chloromesityl oxide* distils at 47° under 12 mm. pressure, decomposes when heated under atmospheric pressure, has a sp. gr. 1.1268 at 11°/4°, and yields a *dichloride* distilling at 104° under 18 mm. pressure. *Methoxymesityl oxide*, $\text{OMe}\cdot\text{C}\cdot\text{Ac}\cdot\text{CMe}_2$, distils at 167—168°, and has a sp. gr. 0.9713 at 11°/4°. *Acetoxymesityl oxide*, $\text{OAc}\cdot\text{C}\cdot\text{Ac}\cdot\text{CMe}_2$, is a colourless liquid distilling at 74° under 12 mm. pressure, and at 177° at atmospheric pressure; it has a sp. gr. 0.9139 at 11°/4°; when boiled for 2—3 hours with 10 per cent. sulphuric acid, it yields Otte and Pechmann's methyl isopropyl diketone (Abstr., 1889, 1137), the *osazone* of which crystallises in sulphur-yellow needles melting at 117°. Methyl isopropyl diketone and *o*-phenylenediamine yield *methylisopropylquinoxaline*, $\text{C}_6\text{H}_4\begin{matrix} \text{N}\cdot\text{CMe} \\ \diagup \quad \diagdown \\ \text{N}\cdot\text{C}\cdot\text{CHMe}_2 \end{matrix}$, which crystallises in plates, melts at 37°, and distils at 264°. Bromomesityl oxide and the sodium derivative of ethyl malonate react but slowly with one another; when they are heated in alcoholic solution for some 70 hours, a 17 per cent. yield of *ethyl mesityl-oxide-malonate* [β -*acetylisobutylene- α -dicarboxylate*], $\text{CMe}_2\cdot\text{C}\cdot\text{Ac}\cdot\text{CH}(\text{CO}_2\text{Et})_2$, is obtained; this distils at 141° under 19 mm. pressure and has a sp. gr. = 1.064 at 11°/4°. *Ethyl $\alpha\beta$ -diacetylpyroterebic acid*, $\text{CMe}_2\cdot\text{C}\cdot\text{Ac}\cdot\text{CHAc}\cdot\text{CO}_2\text{Et}$, distils at 132° under 18 mm. pressure, and gives an indigo-blue coloration with ferric chloride.

J. J. S.

Methyl-2-heptene-4-one-6 and the Synthesis of an Aliphatic Isogeranic Acid. By FERDINAND TIEMANN (*Ber.*, 1900, 33, 559—566).—*a*-Isomethylhepteneone (β -methyl- Δ^7 -heptene- ζ -one) has been described by Barbier and Bouveault (Abstr., 1894, i, 224) and Leser (Abstr., 1898, i, 512). It is best purified by conversion into the sodium hydrosulphonate and after this treatment boils at 178—180° (corr.), and has a sp. gr. 0.8443 at 17°, and a refractive index n_D 1.44275. It forms a semicarbazone melting at 113°. The second carbazone, described by Léser as melting at 100°, is probably a mixture of this with some impurity. The *disemicarbazone*, $\text{C}_{10}\text{H}_{22}\text{O}_2\text{N}_6$, melts at 182°.

When oxidised first with potassium permanganate and then with chromic acid, it yields isovaleric acid, so that the constitution assigned to the compound by Barbier and Bouveault is confirmed. When it is treated with ethyl bromoacetate and zinc, *ethylhydroxydihydroisogeranate*, $\text{CHMe}_2\cdot\text{CH}_2\cdot\text{CH}\cdot\text{CH}\cdot\text{CMe}(\text{OH})\cdot\text{CH}_2\cdot\text{CO}_2\text{Et}$, is formed, which boils at 125—135° under 20 mm. pressure. It has a sp. gr. 0.9385 at 17°, and a refractive index n_D 1.45579. When the free acid is distilled in a vacuum, *isogeraniolene*, $\text{CHMe}_2\cdot\text{CH}_2\cdot\text{CH}\cdot\text{CH}\cdot\text{CMe}\cdot\text{CH}_2$, and *isogeranic acid*, $\text{CHMe}_2\cdot\text{CH}_2\cdot\text{CH}\cdot\text{CH}\cdot\text{CMe}\cdot\text{CH}\cdot\text{CO}_2\text{H}$, are produced. Isogeraniolene boils at 140—142°, and has a sp. gr. 0.7610 at 17° and a refractive index n_D 1.45409. Isogeranic acid boils at 151—154° under a pressure of 14 mm., and has a sp. gr. 0.959 at 17°, and a refractive index n_D 1.49194. On oxidation with potassium permanganate, followed by chromic acid, it yields isovaleric acid.

A. H.

Electro-synthesis of Diketones and Ketones. By HANS HOFER (*Ber.*, 1900, 33, 650—657).—The chief product of the electrolysis of aqueous potassium pyruvate is acetic acid, small quantities of

diacetyl also being formed and carbon dioxide evolved. Potassium lævulate gives rise to $\alpha\delta$ -diacetylbutane in about 50 per cent. of the theoretical yield, a quantity of acetic acid being also produced. From a mixture of potassium pyruvate (1 mol.) and acetate (3 mols.), the products obtained are diacetyl and acetone. Potassium pyruvate and butyrate together yield methyl propyl ketone, which is also obtained from a mixture of potassium lævulate and acetate. A small quantity of $\alpha\beta$ -diacetyethane is formed on electrolysing a mixture of aqueous solutions of potassium pyruvate and lævulate. T. H. P.

Acetylacetone. By FRIEDRICH GACH (*Monatsh.*, 1900, 21, 98—117).—The following new metallic salts of acetylacetone were prepared and analysed:— $\text{Ni}(\text{C}_5\text{H}_7\text{O}_2)_2 + \text{C}_2\text{H}_5\text{OH}$; $\text{Ni}(\text{C}_5\text{H}_7\text{O}_2)_2$; $\text{Co}(\text{C}_5\text{H}_7\text{O}_2)_3$; $\text{Co}(\text{C}_5\text{H}_7\text{O}_2)_2$; $\text{Co}(\text{C}_5\text{H}_7\text{O}_2)_2 + \text{C}_2\text{H}_5\text{OH}$; $\text{Co}(\text{C}_5\text{H}_7\text{O}_2)_2 + \text{COMe}_2$; $\text{Cr}(\text{C}_5\text{H}_7\text{O}_2)_3$; $\text{Mn}(\text{C}_5\text{H}_7\text{O}_2)_3$; $\text{Zn}(\text{C}_5\text{H}_7\text{O}_2)_2$; $\text{Mo}(\text{C}_5\text{H}_7\text{O}_2)_2$. All those which crystallise free from the solvent can be sublimed without decomposition, and their vapour densities were determined by Bleier and Kohn's method (this vol., ii, 192). R. H. P.

Determination of the Inverting Power of Raw Sugar. By LEOPOLD JESSER (*Chem. Centr.*, 1900, i, 106—107; from *Oesterr. Zeit. Zuck.-Ind. Landw.*, 28, 626—628).—The amount of sugar which is decomposed when neutral or alkaline aqueous solutions of raw sugar are boiled, was determined by a method which depends on the property of invert sugar of forming acids of constant acidity when boiled with alkalis and then with excess of acid. The data obtained showed that more sugar is decomposed in alkaline than in neutral solutions. Since the results may not only be affected by the presence of organic compounds having inverting properties, but also by the fact that titration does not necessarily indicate the amount of alkali contained in the product, the amount of sugar inverted was determined by ascertaining its alkalinity before and after boiling for two hours. The difference gives the amount of alkali which is neutralised by the acids formed by boiling the sugar, and those also formed from the invert sugar. From the results, the quantity of invert sugar and of sucrose which has been decomposed can be calculated (compare *Oesterr. Zeit. Zuck.-Ind. Landw.*, 27, 35). The results are tabulated in the original paper, and show that the amount of sugar decomposed differs with the various samples, and bears no relation to the alkalinity. The alkalinity of a raw sugar is therefore neither a criterion of its purity nor of the amount of alkali present. Generally speaking, the amount of sugar decomposed in the case of the crude products was not very different from that obtained in the case of pure sucrose, and in two cases, in which the sugars were distinctly alkaline to phenolphthalein and litmus, the solutions, on boiling, behaved like neutral solutions. Although the purified products showed a marked alkalinity, the amount of sugar decomposed was double that of the crude sugars under similar conditions. One sample of crude sugar, however, gave a result similar to those obtained with purified sugars. The higher inverting powers of the latter must be due to the presence, not only of inverting substances normally contained in the sugar, but also to others formed in the process of manufacture, and possibly by overheating. E. W. W.

Is the Diminution of the Rate of Inversion caused by the Presence of Normal Salts of Inverting Acids, due to the Formation of Esters? By F. STOLLE (*Chem. Centr.*, 1900, i, 439; from *Zeit. Ver. Rübenzuck-Ind.*, 1899, 941—951).—In the action of oxalic acid on raw sugar, as the temperature is raised, each rise of 5° from 5° to 50° causes twice the quantity of sugar to be inverted, but above 50° the increase becomes less. The inverting power and rapidity of action of the equivalent weight of oxalic acid is equal, or nearly equal, to that of the molecular weight of the potassium hydrogen oxalate. When a mixture of equivalent weights of oxalic acid and normal potassium oxalate is used, potassium hydrogen oxalate is not formed, but probably an ester, and it is the presence of this compound which determines the diminution of the rapidity of inversion.

E. W. W.

Colouring Matters contained in "Sugar-Colours," and their Detection. By RUDOLF SCHWEITZER (*Chem. Centr.*, 1900, i, 491; from *Zeit. ges. Brauw.*, 23, 46—48).—The commercial "sugar-colour" preparations differ in their behaviour towards acetic acid and lead acetate; all those prepared by means of alkalis give deep brown precipitates which dissolve in sodium hydroxide solution, forming brown solutions, whilst others are not precipitated, or form only very slight precipitates. A substance, *alkaramel*, $C_{12}H_{11}O_4$, having the properties of an acid, was isolated from caramel, prepared by heating raw sugar with 10 per cent. of sodium carbonate, by precipitating the acetic acid solution with lead acetate and removing the lead from the precipitate. It is a brown powder, leaves no ash, is slightly soluble in dilute alcohol, almost insoluble in water, insoluble in organic solvents, and easily soluble in ammonia or alkalis. Pure sugar-colouring materials, malt extracts, and uncoloured beers do not contain *alkaramel*, but it is characteristic of all alkaline colouring preparations. It has been detected in some beers.

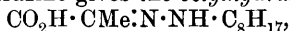
E. W. W.

Action of Silver Oxide and of Hydroxylamine on Bromoamines. By NIC. M. KIJNER (*J. Russ. Phys. Chem. Soc.*, 1899, 31, 872—901, and 948).— γ -Amino-n-heptane, $NH_2 \cdot CHPr^a$, obtained by the reduction of dipropylketoxime with metallic sodium, boils at 140 — 141° under 745 mm. pressure, and has a sp. gr. 0.7671 at $20^{\circ}/0^{\circ}$. The *hydrochloride* forms thin, prismatic crystals melting at 247° , and the *platinichloride* crystallises in anhydrous, golden leaflets. The amine combines with phenylthiocarbimide, forming the corresponding *thiocarbanilide*, $NHPh \cdot CS \cdot NH \cdot C_7H_{15}$, which crystallises in needles melting at 75° .

On brominating the amine and acting on the product with silver oxide, the *heptylhydrazine*, $N_2H_3 \cdot CHPr^a_2$, is formed; it boils undecomposed at 190 — 192° under the ordinary pressure, and has a sp. gr. 0.8545 at $0^{\circ}/0^{\circ}$. It quickly oxidises in the air with evolution of gas, and reduces an ammoniacal solution of silver oxide in the cold. With pyruvic acid, it yields the *heptylhydrazone*, $CO_2H \cdot CMe \cdot N_2H \cdot C_7H_{15}$, which is readily soluble in benzene and in light petroleum, from which it separates in slender needles melting at 57 — 58° ; it is readily soluble in alkalis, and is reprecipitated unchanged on the addition of acids. The hydrazine combines with phenylthiocarbimide, yielding the *thio-*

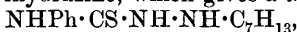
carbanilide, $\text{NHPh}\cdot\text{CS}\cdot\text{NH}\cdot\text{NH}\cdot\text{C}_7\text{H}_{15}$, which separates from alcohol in beautiful plates melting at 122° .

By reducing methyl hexyl ketone oxime, or by the action of ammonium formate on methyl hexyl ketone, β -amino-octane is obtained; it boils at $165\text{--}166^\circ$ under 758 mm. pressure, and has a sp. gr. $0\cdot7721$ at $20^\circ/0^\circ$. Jahn gave the boiling point $162\cdot5^\circ$, and Konowaloff found that it boils at $163\text{--}164^\circ$ under 754 mm. pressure, and has a sp. gr. $0\cdot7745$ at $20^\circ/0^\circ$. Along with the octylamine obtained by the second of the above methods, there is found a small quantity of *dioctylamine*, $\text{NH}(\text{C}_8\text{H}_{17})_2$, which boils at $281\cdot5^\circ$ under 739 mm. pressure, and has the sp. gr. $0\cdot7948$ at $20^\circ/0^\circ$; by the action of sodium nitrite on its hydrochloride, the *nitroso*-compound, $\text{NO}\cdot\text{N}(\text{C}_8\text{H}_{17})_2$, is obtained. By the action of silver oxide on the bromo-derivative of β -amino-octane, *methyl hexyl ketone octylhydrazone*, $\text{C}_8\text{H}_{16}\cdot\text{N}\cdot\text{NH}\cdot\text{C}_8\text{H}_{17}$, and *octylhydrazine*, $\text{CH}_2\text{Me}\cdot[\text{CH}_2]_4\cdot\text{CHMe}\cdot\text{NH}\cdot\text{NH}_2$, are formed; the latter boils at $210\text{--}215^\circ$, oxidises in the air with evolution of gas, and, on gently warming, reduces an ammoniacal solution of silver oxide. The octylhydrazine combines with phenylthiocarbimide, yielding the corresponding *thiocarbanilide*, $\text{NHPh}\cdot\text{CS}\cdot\text{NH}\cdot\text{NH}\cdot\text{C}_8\text{H}_{17}$, which crystallises from ethyl acetate in slender needles melting at 116° . With pyruvic acid, octylhydrazine gives the *octylhydrazone*,



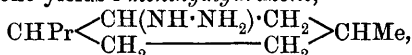
which melts at 39° .

The interaction of silver oxide and 1-methyl-3-bromoaminocyclohexane yields 1:3-methylcyclohexenone and a small quantity of 1:3-methylcyclohexylhydrazine, which gives a *thiocarbanilide*,



crystallising from alcohol in colourless, rhombic plates melting at $137\text{--}138^\circ$.

Silver oxide reacts with *l*-bromomenthylamine, forming menthanementhylhydrazone, which melts at 93° and in benzene solution has a specific rotation $[\alpha]_D = -378\cdot1^\circ$. When boiled with hydrochloric acid, this hydrazone yields 1-menthylhydrazone,



which is a thick, colourless liquid boiling at $240\text{--}242^\circ$ under 761 mm. pressure; it oxidises in the air with evolution of gas. With phenylthiocarbimide, it yields *menthylhydrazylphenylthiocarbanilide*, $\text{NHPh}\cdot\text{CS}\cdot\text{NH}\cdot\text{NH}\cdot\text{C}_{10}\text{H}_{19}$, melting at 160° ; this is insoluble in alkalis, and in benzene solution has the specific rotation $[\alpha]_D = -49\cdot10^\circ$.

Concentrated nitric acid oxidises menthanementhylhydrazone at the ordinary temperature, yielding a *substance*, $(\text{C}_{20}\text{H}_{38}\text{ON}_2)$, probably $\text{ON}_2(\text{C}_6\text{H}_9\text{MePr})_2$, which crystallises from aqueous alcohol in slender, colourless, silky needles, melts at $84\text{--}84\cdot5^\circ$, is readily volatile in a current of steam, has the normal molecular weight in freezing benzene, and in benzene solution has a specific rotation $[\alpha]_D = -177^\circ$ at 22° . When heated with hydrochloric acid, it is resolved into hydrazine and menthone, and with concentrated hydriodic acid it yields menthyl iodide and a menthylamine salt. Zinc dust in dilute aqueous solution reduces it to menthanementhylhydrazone, which has a specific rotation $[\alpha]_D = -406^\circ$, a value considerably higher than that ($-378\cdot1^\circ$) of the original substance.

Dimethylamine, $\text{NH}(\text{C}_{10}\text{H}_{19})_2$, obtained together with *d*-menthylamine when ammonium formate is heated with menthone, is a thick liquid with a faint smell; it boils at $220\text{--}222^\circ$ under 45 mm. pressure, and at the ordinary pressure distils almost unchanged at above 300° . The hydrochloride gives with potassium nitrite a liquid *nitrosamine*. *d*-Menthylamine boils at 206° , has the sp. gr. 0.8589 at $20^\circ/0^\circ$, and the specific rotation $[\alpha]_D = +14.87^\circ$ (Wallach gives 14.71°). The action of silver oxide on the bromo-derivative of *d*-menthylamine yields menthone and *menthazine*, $\text{N}_2(\text{C}_6\text{H}_8\text{MePr})_2$, which crystallises from aqueous alcohol in pale yellow needles melting at $50\text{--}52^\circ$; it is also obtained on warming menthone with hydrazine hydrate and anhydrous barium oxide. On warming with dilute hydrochloric acid, it yields hydrazine hydrochloride. T. H. P.

Some Halogen Derivatives of Hexamethylenetetramine (Urotropine). By M. HÖHNEL (*Arch. Pharm.*, 1899, **237**, 692—698).—The following crystalline derivatives of hexamethylenetetramine were prepared by mixing the base, or a derivative of it, with the halogen, &c., usually in alcoholic, but sometimes in chloroform or aqueous, solution. The perhaloids tend to lose the excess of halogen in the air.

Perbromide, $(\text{CH}_2)_6\text{N}_4\text{Br}_4$. *Methobromide dibromide*, $(\text{CH}_2)_6\text{N}_4\text{EtBr}_2$. *Diiodide*, $(\text{CH}_2)_6\text{N}_4\text{I}_2$. *Periodide*, $(\text{CH}_2)_6\text{N}_4\text{I}_4$. *Methiodide diiodide*, $(\text{CH}_2)_6\text{N}_4\text{MeI}_2$. *Hydriodide diiodide*, $(\text{CH}_2)_6\text{N}_4\text{HI}_2$. *Diiodide mercuriiodide*, $(\text{CH}_2)_6\text{N}_4\text{I}_2 + 2\text{HgI}_2$; *diiodide mercurichloride*, $(\text{CH}_2)_6\text{N}_4\text{I}_2 + 2\text{HgCl}_2$. *Chloriiodide*, $(\text{CH}_2)_6\text{N}_4\text{ICl}$. *Chloral*, $(\text{CH}_2)_6\text{N}_4 + \text{CCl}_3\cdot\text{CHO} + 2\text{H}_2\text{O}$ (compare German Patent, 87933). *Bromal*, $(\text{CH}_2)_6\text{N}_4 + \text{CBr}_3\cdot\text{CHO} + 2\text{H}_2\text{O}$. C. F. B.

Polyaspartic Acids. By HUGO SCHIFF (*Gazzetta*, 1900, **30**, i, 8—25; and *Annalen*, 1900, **310**, 301—305. Compare Abstr., 1899, i, 195 and 674).—[With GIULIO MARZICHI.]—When octoaspartide is heated with ammonia in ethereal solution in sealed tubes at 100° , *octoaspartotetramide*, $\text{C}_{32}\text{H}_{26}\text{O}_{17}\text{N}_8 + 4\text{NH}_3$, is obtained as a yellowish powder; heated at 120° or placed in a vacuum over sulphuric acid, it loses ammonia and yields the triamide. The latter neutralises rather more than 2 mols. of potash and gives two *copper* compounds, having the composition $\text{C}_{32}\text{H}_{41}\text{O}_{22}\text{N}_{11}\text{Cu}_2$ and $\text{C}_{32}\text{H}_{35}\text{O}_{27}\text{N}_{11}\text{Cu}_5$ respectively.

Tetra-aspartide loses all its water at $120\text{--}130^\circ$, and at a higher temperature yields *diaspartidodiaspartic acid*, $\text{C}_{16}\text{H}_{18}\text{O}_{11}\text{N}_4$, which absorbs ammonia with development of heat, forming a *tetrammonium* salt, $\text{C}_{16}\text{H}_{18}\text{O}_{11}\text{N}_4 + 4\text{NH}_3$, and this, when placed in a vacuum over sulphuric acid and finally heated at 120° , gives the *diammonium* salt, $\text{C}_{16}\text{H}_{18}\text{O}_{11}\text{N}_4 + 2\text{NH}_3$. The latter is soluble in water, giving a neutral solution, from which it is precipitated by the addition of acetic acid; on heating the solution for some time, it becomes acid, and on then evaporating in a vacuum it deposits an almost colourless, glassy, and slightly hygroscopic compound of the composition $\text{C}_{16}\text{H}_{22}\text{O}_{12}\text{N}_4 + 2\text{NH}_3$, which dissolves in water, and is not precipitated by acetic acid.

On heating ammonium tetra-aspartate at $200\text{--}210^\circ$, it loses all its ammonia and is converted into octoaspartide.

[With MARIO BETTI.]—*Diisoamylamineoctoaspartide*, $C_{32}H_{26}O_{17}N_8 + 2C_5H_{13}N$, has a yellowish colour, and is insoluble in all solvents. *Hexaisoamylamineoctoaspartide*, $C_{32}H_{26}O_{17}N_8 + 6C_5H_{13}N$, is a yellowish substance which partially dissolves in concentrated potassium hydroxide solution, giving an odour of isoamylamine; after standing for some time, this solution gives the biuret reaction. It is slightly soluble in ammonia and partially so in dilute acetic acid. *Heptaisoamylamineoctoaspartide*, $C_{32}H_{26}O_{17}N_8 + 7C_5H_{13}N$, has an almost white, crystalline appearance, and with potash gives an odour of isoamylamine, and, after a time, the biuret reaction; it is insoluble in the ordinary solvents and partially melts at about 220° .

Tetrazobenzylamineoctoaspartide, $C_{32}H_{26}O_{17}N_8 + 4C_7H_9N$, is a yellow substance which does not melt; it is fairly soluble in cold potash solution or hot ammonia solution, and gives the biuret reaction. *Octobenzylamineoctoaspartide* has a yellow colour and dissolves slightly in potash, the solution giving a faint biuret reaction; it is almost insoluble in alcohol or dilute acids; fusion commences at 205° , but is never complete.

Tetra-m-tolylenediamineoctoaspartide, $C_{32}H_{26}O_{17}N_8 + 4C_7H_{10}N_2$, is a brownish-yellow, amorphous substance slightly soluble in acetic acid or potash, the colour of the solution not allowing the biuret reaction to be detected; when the solution is warmed with potash, ammonia is evolved, and when treated with furfuraldehyde and acetic acid, an orange-red coloration is produced, indicating the presence of free aromatic amino-groups; it softens at 250° , and, at higher temperatures, decomposes. It yields two copper compounds; the first, having the composition $C_{60}H_{72}O_{23}N_{16}Cu_3$, is a greyish-green substance, and the other, $C_{60}H_{70}O_{21}N_{16}Cu_2$, has a green colour and darkens and decomposes at above 200° .

Dibenzidinedi-octoaspartide, $C_{32}H_{26}O_{17}N_8 + 2C_{12}H_{12}N_2$, is resinified by acids or potash, dissolves slightly in ammonia solution, and gives the biuret reaction. *Tribenzidinedi-octoaspartide* gives the biuret reaction, and answers to the test for free aromatic amino-groups; it is slightly soluble in ammonia or dilute potash solution, but insoluble in boiling concentrated hydrochloric acid, and at high temperatures decomposes without melting. It forms a yellowish-green copper salt of the composition $C_{68}H_{80}O_{31}N_{14}Cu_5$. *Pentabenzidinedi-octoaspartide* does not melt, and is insoluble in potash or hydrochloric acid. By treating the tribenzidine derivative with a further quantity of benzidine, a compound of the composition $C_{32}H_{26}O_{17}N_8 + 5C_{12}H_{12}N_2 - 4NH_3$ is obtained.

With β -naphthylamine, octoaspartide gives *tetranaphthyl-octonaphthylamineoctoaspartide*, $C_{32}H_{26}O_{17}N_8 + 12C_{10}H_9N - 4NH_3$, which is obtained in yellowish flocks by pouring its alcoholic solution into a large volume of very dilute hydrochloric acid; it melts sharply at 165 – 166° and is soluble in potash, but does not give the biuret reaction. T. H. P.

Preparation of Carbamide from Guanidine. By HUGO FLEMING (*Chem. Zeit.*, 1900, 24, 56).—Carbamide may be readily obtained in a pure state by the action of barium hydroxide on the boiling aqueous solution of a guanidine salt, as first suggested by Baumann (*Ber.*, 1873, 6, 1376). E. G.

Pentabromobenzene. By PAUL JACOBSON and ARTHUR LOEB (*Ber.*, 1900, 33, 702—706).—Pentabromoaniline sinters at 254°, melts at 256—257° (261—262°, corr.), not at 225°, as stated by Hantzsch and Smythe (*Ber.*, 1900, 33, 505), and by elimination of the amino-group yields pentabromobenzene, which melts at 159—160° (Hantzsch and Smythe, 158°). Neither Kekulé (*Annalen*, 1866, 137, 171), Bässmann (*Annalen*, 1878, 191, 208), nor Diehl (*Ber.*, 1878, 11, 191), who have described pentabromobenzene as melting above 240°, were dealing with the true substance; that obtained by the authors on nitration yields *pentabromonitrobenzene*, which crystallises from alcohol in white needles melting at 234—235° (corr.) (Jackson and Bancroft, *Abstr.*, 1890, 982, describe “pentabromonitrobenzene” as melting at 248°), and on reduction with iron and acetic acid yields pentabromoaniline. Two of the bromine atoms of pentabromobenzene are removed on warming with alcoholic sodium ethoxide.

W. A. D.

Oxidation of Aromatic Iodides. By EUGEN BAMBERGER and ADOLF HILL (*Ber.*, 1900, 33, 533—536).—Caro's reagent (*Zeit. angew. Chem.*, 1898, 845) oxidises aliphatic amines of the type $R \cdot CH_2 \cdot NH_2$ to the corresponding oximes, $R \cdot CH : N \cdot OH$, β -alkylhydroxylamines probably being formed initially; methylamine yields formoxime and benzylamine *syn*- and *anti*-benzaloximes. Details of this work will be published later.

The same reagent oxidises aromatic iodides, $C_6H_4R \cdot I$, to the corresponding iodoxy-compounds, $C_6H_4R \cdot IO_2$; in the present paper, the oxidation of iodobenzene, and *o*-, *m*-, and *p*-iodotoluene is dealt with. *m*-Iodoxytoluene, $C_7H_7O_2I$, the only new compound described, crystallises in white, lustrous needles, explodes between 214° and 221°, and is converted by hydrogen peroxide into *m*-iodotoluene (compare Willgerodt, *Abstr.*, 1893, i, 505).

W. A. D.

Gradual Electrolytic Reduction of Nitrobenzene with Limited Cathode Potential. By FRITZ HABER (*Zeit. Elektrochem.*, 1898, 4, 506—513).—Besides current strength, duration of current, and nature of the electrodes, the fall of potential at the electrodes is an important factor in electrolytic oxidation and reduction processes. A platinum electrode in an alkaline alcoholic solution of nitrobenzene shows the potential difference -0.72 volt; with cathode polarisation, this falls to the value -1.29 volts, when hydrogen is liberated. By regulating the potential difference between these values, various grades of reducing energy are available.

With a potential greater than -0.93 volt, the chief reduction product of nitrobenzene is azoxybenzene, accompanied by small quantities of azobenzene, hydrazobenzene, and aniline. Special experiments showed that hydrazobenzene in alkaline alcoholic solution is further reduced only with great difficulty, and the author accordingly regards the direct line of reduction as being $C_6H_5 \cdot NO_2 \rightarrow C_6H_5 \cdot NO \rightarrow C_6H_5 \cdot NH \cdot OH \rightarrow C_6H_5 \cdot NH_2$, the nitrosobenzene and the phenylhydroxylamine reacting to form azoxybenzene. The presence of nitrosobenzene was confirmed: that it cannot be isolated in quantity is due to the fact that the potential difference between platinum and an alkaline alcoholic solution of nitrosobenzene is only -0.48 volt. The hydrazo-

benzene obtained appears to be the reduction product of the secondarily formed azoxybenzene.

The reduction of nitrobenzene in acid alcoholic solution leads to the products azoxybenzene, benzidine, aniline, *p*-aminophenol, and phenetidine; the presence of the two latter compounds points to an intermediate formation of phenylhydroxylamine, which by mere standing in acid alcoholic solution yields phenetidine. The benzidine is formed as the reduction product, not of the phenylhydroxylamine, but of the azoxybenzene; the formation of this compound from nitrosobenzene and phenylhydroxylamine takes place in acid alcoholic solution with much less rapidity than in alkaline alcoholic solution.

The nature of the whole process depends on the energy of reduction as determined by the cathode potential, and on the velocity of the secondary chemical reactions involved. J. C. P.

Electrolytic Reduction of Nitrobenzene. By FRITZ HABER and CARL SCHMIDT (*Zeit. physikal. Chem.*, 1900, 32, 271—287).—The results obtained by Haber (see previous abstract) are confirmed and supplemented.

Phenylhydroxylamine cannot be obtained from caustic alkali solutions, owing to its instability in that medium, but it is readily isolated by the electrolytic reduction of nitrobenzene in ammoniacal alcoholic solution. The azobenzene previously detected in the reduction of nitrobenzene in alkaline alcoholic solution is not due to the reduction of the azoxybenzene, but is formed by the action of nitrobenzene on hydrazobenzene.

The authors also discuss Möller's observation (*Abstr.*, 1900, i, 27), that phenylcarbylamine is produced in the electrolysis of alkaline alcoholic solutions of nitrobenzene, and point to the possibility of its being formed from the products at the cathode. J. C. P.

Benzenesulphonamides of Primary Bases, and the Use of Hinsberg's Reaction for Determination of Structure. By PAUL DUDEN (*Ber.*, 1900, 33, 477—481).—Whilst benzenesulphonethylamide is dissolved to the extent of 82 per cent. by one equivalent of *N* sodium hydroxide, and to the extent of 94 per cent. by 3 mols., benzenesulphonheptylamide and benzenesulphoncamphylamide are not acted on by alkalis, except in concentrated solutions, when they are converted into the slightly soluble sodium salts; almost the whole of the latter amides can, however, be recovered by extracting the alkaline solution with ether, and these amides are therefore practically neutral substances when compared with the benzenesulphonamides from methylamine, aniline, &c.; it is suggested that perhaps they are 'pseudo-acids,' $C_6H_5 \cdot SO_2 \cdot NHR$, which are converted into true acids, $C_6H_5 \cdot SO(OH) \cdot NR$, by strong alkali. The author concludes that Hinsberg's reaction cannot be trusted in determining the constitution of bases. T. M. L.

1-Naphthyliodochloride, 1-Iodosonaphthalene, 4:4'-Diiodo-1:1'-dinaphthyl, 1-Naphthylphenyliodonium Hydroxide and Derivatives thereof. By CONRAD WILLGERODT and PETER SCHLÖSSER (*Ber.*, 1900, 33, 692—702).—1-Naphthyliodochloride (*Abstr.*, 1894, i, 295), $C_{10}H_7ICl_2$, prepared by passing chlorine into a well-cooled

solution of 1-iodonaphthalene in glacial acetic acid or ether, or by dissolving 1-iodosonaphthalene in dilute hydrochloric acid, separates in long, well-formed needles, and rapidly decomposes; the products obtained by the first method are the more unstable, decomposing at 34° or 49° respectively, according to the solvent used in the preparation, whilst that obtained from 1-iodosonaphthalene decomposes at 56° , or after being kept for about 20 hours. In chloroform solution, the decomposition yields iodine, 1-chloronaphthalene tetrachloride, and 1:4-chloroiodonaphthalene; the latter is a pale yellow oil which boils above 300° , is more stable than 1-iodonaphthalene, and with chlorine yields an unstable *iodochloride* convertible by sodium hydroxide into a moderately stable iodoso-compound.

1-Iodosonaphthalene (*loc. cit.*), when dissolved in glacial acetic acid, yields the *acetate*, $C_{10}H_7 \cdot I(OAc)_2$, which separates in short, white needles and decomposes at 192° (corr.).

The *basic nitrate*, $C_{10}H_7 \cdot I(OH)NO_3$, prepared from 1-iodosonaphthalene and dilute nitric acid, is decomposed by all solvents except chloroform; from the latter, it separates in slender, yellow needles which decompose at 94° . The *basic sulphate*, $(C_{10}H_7 \cdot I \cdot OH)_2SO_4$, is unstable, decomposing explosively. 1-Iodosonaphthalene in contact with water at the ordinary temperature or with steam yields 1-iodonaphthalene, iodic acid, and probably a hydrocarbon (? a dinaphthyl). Neither 1-iodoxy-naphthalene nor 1:1-dinaphthylidonium iodide could be prepared.

When the foregoing basic sulphate is heated with either glacial acetic acid or chloroform at 37° , vigorous action occurs and 4:4'-*diiodo-1:1'-dinaphthyl* is formed; this crystallises in lustrous prisms, melts at 238.6° (corr.), and on reduction with sodium amalgam in absolute alcohol yields *aa-dinaphthyl* (m. p. 160.5° corr.). When 1-iodosonaphthalene is dissolved in well-cooled concentrated sulphuric acid, practically none of the expected iodonium compound is formed, the principal product being 4:4'-*diiodo-1:1'-dinaphthyl*; phosphoric oxide acts similarly. The *iodo-iodochloride*, $C_{20}H_{12} \cdot I \cdot ICl_2$, prepared from 4:4'-*diiodo-1:1'-dinaphthyl* by the action of chlorine, is a yellow, amorphous powder which does not decompose at a definite temperature; the *compound* $(C_{10}H_6 \cdot ICl_2)_2$ crystallises from chloroform in beautiful, long needles and decomposes at 124° .

Phenyl- α -naphthylidonium hydroxide, $C_{10}H_7 \cdot IPh \cdot OH$, cannot be prepared by Victor Meyer's method from 1-iodosonaphthalene, iodoxybenzene and moist silver oxide, but is obtained from its chloride; it exists only in aqueous solution, to which it imparts strongly alkaline properties. The *chloride*, $C_{10}H_7 \cdot IPh \cdot Cl$, crystallises from water in slender, white needles, and melts at 168° ; the corresponding *bromide* is similar and melts at 179° , whilst the *iodide* is very sparingly soluble in water, and forms slender, yellow needles which explode at 176° . The crystalline *nitrate*, $C_{10}H_7 \cdot IPh \cdot NO_3$, decomposes at $187-188^{\circ}$; the *platinichloride*, at $145-150^{\circ}$; whilst the *mercurichloride* melts at 145° .

W. A. D.

Synthesis of Homologues of Diphenylmethane by Oxidation of Toluene and its Homologues. By MAX WEILER (*Ber.*, 1900, 33, 464—471).—On oxidising toluene with manganese dioxide

and a mixture of sulphuric and acetic acids, a mixture of products results. The fraction boiling from 130—270° contains a little benzaldehyde, but consists chiefly of benzyl acetate. The fraction boiling at 270—300°, when oxidised with chromyl chloride, gives a little anthracene, indicating the presence of dihydroanthracene in the original oil, but chiefly a ketonic mixture of phenyl *p*-tolyl ketone, with an oil which is shown to contain a considerable amount of phenyl *o*-tolyl ketone, since it gives anthraquinone when oxidised with lead oxide; dibenzyl is not present in the original oil, since this would have been isolated from the oxidation product as dibenzyl, stilbene, or benzaldehyde. On oxidation with potassium permanganate, the same fraction gives benzoic, terephthalic, *o*-phthalic, and *p*- and *o*-benzoylbenzoic acids, but not *pp*-diphenyldicarboxylic acid, showing that *pp*-ditolyl is not present in the original oil.

Oxidation of mesitylene with manganese dioxide and sulphuric acid (62 per cent.) gave *s*-dimethylbenzaldehyde (about 31 per cent. of the theoretical amount), mesitylenic acid (3 per cent.), a hydrocarbon melting at 132—133° (0·9 per cent.), pentamethyldiphenylmethane (11·5 per cent.), and higher hydrocarbons. With manganese dioxide, sulphuric and acetic acids, there were produced traces of *s*-dimethylbenzaldehyde, pentamethyldiphenylmethane (13·6 per cent. of theoretical), the hydrocarbon melting at 132—133°, and higher hydrocarbons, but no *s*-dimethylbenzyl alcohol. The hydrocarbon, melting at 132—133°, crystallises in square plates or in four-sided prisms, boils undecomposed at 350°, does not combine with picric acid, is not attacked by ferric chloride, but is oxidised completely by chromic acid, and does not give fluorescent solutions; it is probably 1:3:5:7-tetramethyldihydroanthracene, corresponding with the dihydroanthracene formed in the oxidation of toluene.

T. M. L.

New Aromatic Hydrocarbon, $C_{24}H_{18}$, from Mineral Oil. By JOSEF KLAUDY and ISIDOR FINK (*Monatsh.*, 1900, 21 118—136).—The authors have isolated a new aromatic hydrocarbon, $C_{24}H_{18}$, which they name *crackene*, from the so-called red pitch, which is obtained as a sticky sublimate when the distillation of Saxon lignite tar is conducted at a high temperature. After some months, this sublimate becomes hard, and by crystallisation from benzene or ethyl acetate, yielded the hydrocarbon in the form of yellow leaflets with a green fluorescence; it melts at 308°, can be sublimed, and boils with decomposition at about 500°.

Dibromocrackene, $C_{24}H_{16}Br_2$, obtained by the action of bromine dissolved in chloroform on crackene, forms small, dark yellow leaflets melting at 141°. Chromic acid oxidises the hydrocarbon to *crackenequinone*, which forms dark red, microscopic crystals melting at 208°, and is probably an *o*-diketone. *Dinitrocrackene* is a dark red powder, and *tetranitrocrackene* a bright yellow powder, which melts and explodes below 100°.

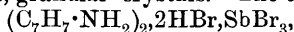
Dihydrooxycrackene, $C_{24}H_{16}(OH)_2$, formed by the action of aqueous sodium hydroxide on dinitrocrackene, is a brown, amorphous mass. The constitution of crackene has not yet been determined; it is probably identical with the hydrocarbon, $(C_4H_3)_x$, obtained by Divers

and Nakamura from Japanese petroleum (Trans., 1885, 924), and with Schmidt and Schultz's benzerythrene (Abstr., 1878, 323; 1881, 435) R. H. P.

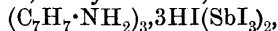
Double Halogen Salts of Antimony with Aniline and the Toluidines. By HOWARD H. HIGBEE (*Amer. Chem. J.*, 1900, 23, 150—173).—*Trianiline antimoniochloride*, $(\text{NH}_2\text{Ph})_3, 3\text{HCl}, \text{SbCl}_3 + \text{H}_2\text{O}$, forms thick, colourless, monoclinic prisms, which, on exposure to the air, become opaque, and of a greenish colour; on gently heating, it decomposes, with loss of hydrogen chloride. *Aniline antimoniochloride*, $\text{NH}_2\text{Ph}, \text{HCl}, \text{SbCl}_3 + \text{H}_2\text{O}$, forms long, thin, colourless plates. The corresponding bromides could not be obtained; *dianiline antimonio-bromide*, $(\text{NH}_2\text{Ph})_2, 2\text{HBr}, \text{SbBr}_3$, forms canary-yellow, lath-shaped, orthorhombic crystals, which are stable in the air; *tetraniline anti-moniobromide*, $(\text{NH}_2\text{Ph})_4, 4\text{HBr}, \text{SbBr}_3 + \text{H}_2\text{O}$, forms transparent, tabular, light yellow, orthorhombic crystals with a perfect cleavage, which, on keeping, become opaque. Of the *aniline antimonioiodides* (1), $\text{NH}_2\text{Ph}, \text{HI}, \text{SbI}_3$, crystallises in stable, minute, scarlet octahedra; (2), $(\text{NH}_2\text{Ph})_3, 3\text{HI}, (\text{SbI}_3)_2$, forms slender, carmine needles, whilst (3), $(\text{NH}_2\text{Ph})_4, 4\text{HI}, \text{SbI}_3$, separates in golden-yellow plates, which, on draining, become orange-red.

From *o*-toluidine only one *chloride*, $(\text{C}_7\text{H}_7\cdot\text{NH}_2)_2, 2\text{HCl}, \text{SbCl}_3$, can be obtained; the *bromide*, $(\text{C}_7\text{H}_7\cdot\text{NH}_2)_3, 3\text{HBr}, \text{SbBr}_3$, forms light yellow, stunted prisms. Of the *iodides*, (1), $\text{C}_7\text{H}_7\cdot\text{NH}_2, \text{HI}, \text{SbI}_3$, crystallises in short, brick-red needles; (2), $(\text{C}_7\text{H}_7\cdot\text{NH}_2)_3, 3\text{HI}, (\text{SbI}_3)_2$, forms irregular, bronze-coloured leaflets.

m-Toluidine Salts.—*Chlorides*: (1), $(\text{C}_7\text{H}_7\cdot\text{NH}_2)_3, 3\text{HCl}, \text{SbCl}_3$, crystallises in thin, colourless, orthorhombic tables; (2), $(\text{C}_7\text{H}_7\cdot\text{NH}_2)_2, 2\text{HCl}, \text{SbCl}_3 + \text{H}_2\text{O}$, forms colourless, granular crystals. The *bromide*,

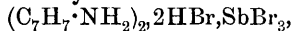


forms long, pale yellow, silky needles; the *iodide*,



lustrous, brick-red prisms.

p-Toluidine Salts.—*Chlorides*: (1), $(\text{C}_7\text{H}_7\cdot\text{NH}_2)_2, 2\text{HCl}, \text{SbCl}_3 + \frac{1}{2}\text{H}_2\text{O}$, forms long, colourless, silky needles; (2), $(\text{C}_7\text{H}_7\cdot\text{NH}_2)_3, 3\text{HCl}, \text{SbCl}_3 + \text{H}_2\text{O}$, colourless, granular crystals. *Bromides*: (1),



anhydrous, and also with $1\text{H}_2\text{O}$; (2), $(\text{C}_7\text{H}_7\cdot\text{NH}_2)_3, 3\text{HBr}, \text{SbBr}_3$; (3), $(\text{C}_7\text{H}_7\cdot\text{NH}_2)_4, 4\text{HBr}, \text{SbBr}_3$. In dry air, these compounds are canary-yellow, but when exposed to a damp atmosphere they become snow-white. The *iodide*, $\text{C}_7\text{H}_7\cdot\text{NH}_2, \text{HI}, \text{SbI}_3$, forms light orange, blunt, prismatic crystals, and darker orange-coloured needles. W. A. D.

Action of Formaldehyde on Anilides. By CARL GOLDSCHMIDT (*Chem. Zeit.*, 1900, 24, 97).—When formanilide is dissolved in formaldehyde solution (40 per cent.) and water added, an unstable oil is precipitated which yields a sodium salt; but if the solution is left for 24 hours in the presence of hydrochloric or sulphuric acid, and then treated with sodium hydroxide, a white, amorphous base, *anhydro-p-formaminobenzyl alcohol*, $\text{C}_{16}\text{H}_{14}\text{O}_2\text{N}_2$, separates, which is easily

soluble in chloroform, yields salts, and combines with benzoyl chloride.

Formyl-*o*-anisidine yields a similar compound.

E. G.

ψ -Carbamides. By ERNST MENNE (*Ber.*, 1900, 33, 657—665. Compare Gabriel, *Abstr.*, 1889, 848, &c.).—When a benzene solution of bromoethylamine, prepared by shaking the hydrobromide with 33 per cent. potassium hydroxide solution, is mixed with phenylcarbimide, *phenylbromoethylcarbamide*, $\text{NPh}\cdot\text{CO}\cdot\text{NH}\cdot\text{CH}_2\cdot\text{CH}_2\text{Br}$, melting at $106\text{--}107^\circ$, is formed; when this is boiled with water, it is transformed into the hydrobromide of *N*-phenylethylene- ψ -carbamide,

$\text{NPh}\cdot\text{C}\begin{smallmatrix} \text{O}\cdot\text{CH}_2 \\ \text{N}\cdot\text{CH}_2 \end{smallmatrix}$ (Gabriel, *Abstr.*, 1896, i, 121), the *picrate* of which melts and decomposes at 175° . When phenylthiocarbimide is used instead of phenylcarbimide, the hydrobromide of the phenylethylene- ψ -thiocarbamide is obtained at once, no intermediate product being formed; at the same time, a compound of the ψ -thiocarbamide with

phenylthiocarbimide, $\text{NPh}\cdot\text{CS}\cdot\text{NPh}\cdot\text{C}\begin{smallmatrix} \text{S}\cdot\text{CH}_2 \\ \text{N}\cdot\text{CH}_2 \end{smallmatrix}$, melting at 113° , is formed. The *picrate*, *aurichloride*, and *platinichloride* of the ψ -thiocarbamide melt at $198\text{--}202^\circ$, $140\text{--}142^\circ$, and $199\text{--}202^\circ$ respectively; by treating it with methyl iodide, the *hydriodide* of *phenylmethylethylene- ψ -thiocarbamide*, melting at 165° , is obtained; the corresponding base was only obtained as an oil.

By mixing aromatic bases, NH_2R , with allylcarbimide in benzene solution, allylcarbamides, $\text{NHR}\cdot\text{CO}\cdot\text{NH}\cdot\text{CH}_2\cdot\text{CH}:\text{CH}_2$, are obtained; when these are heated at 100° with fuming hydrochloric acid, β -chloropropylcarbamides, $\text{NHR}\cdot\text{CO}\cdot\text{NH}\cdot\text{CH}_2\cdot\text{CHMeCl}$, are formed, and, with

alkalis, can be converted into ψ -carbamides, $\text{NHR}\cdot\text{C}\begin{smallmatrix} \text{O}\cdot\text{CHMe} \\ \text{N}\cdot\text{CH}_2 \end{smallmatrix}$. The compounds obtained and analysed are enumerated below, with their melting points: *phenylallylcarbamide*, $115\cdot5^\circ$; *phenyl- β -chloropropylcarbamide*, 121° ; *N*-phenylpropylene- ψ -carbamide, 132° , *picrate*, $166\text{--}168^\circ$, *aurichloride*, 168° , *platinichloride* [$\text{R}=\text{Ph}$]. Starting with methylaniline instead of aniline, *phenylmethylpropylene- ψ -carbamide* is obtained as an oil, *picrate*, $156\text{--}157^\circ$. *o*-Tolylallylcarbamide, 152° ; *o*-tolyl- β -chloropropylcarbamide, $95\text{--}97^\circ$; *o*-tolylpropylene- ψ -carbamide, 80° , *picrate*, $168\text{--}170^\circ$, *aurichloride*, $140\text{--}142^\circ$ [$\text{R}=\text{C}_6\text{H}_4\text{Me}$ (*o*)]. *m*-Tolylallylcarbamide, 115° ; *m*-tolyl- β -chloropropylcarbamide; *m*-tolylpropylene- ψ -carbamide, $86\text{--}87^\circ$, *picrate*, *aurichloride*, 115° , *platinichloride*, 157° [$\text{R}=\text{C}_6\text{H}_4\text{Me}$ (*m*)]. *p*-Tolylallylcarbamide, 139° ; *p*-tolyl- β -chloropropylcarbamide, 138° ; *p*-tolylpropylene- ψ -carbamide, 118° , *picrate*, 184° , *aurichloride*, $167\text{--}168^\circ$, *platinichloride*, 185° [$\text{R}=\text{C}_6\text{H}_4\text{Me}$ (*p*)]. *a*-m-Xylallylcarbamide, 165° ; *a*-m-xyl- β -chloropropylcarbamide; *a*-m-xylpropylene- ψ -carbamide, $86\text{--}88^\circ$, *picrate*, $172\text{--}174^\circ$, *aurichloride*, *platinichloride*, [$\text{R}=\text{C}_6\text{H}_3\text{Me}_2$ (2:4)]. *o*-Anisylallylcarbamide, 112° ; *o*-anisyl- β -chloropropylcarbamide, 103° ; *o*-anisylpropylene- ψ -carbamide, $87\text{--}88^\circ$, *aurichloride*, 129° , *platinichloride*, $160\text{--}161^\circ$ [$\text{R}=\text{C}_6\text{H}_4\cdot\text{OMe}$ (*o*)]. *m*-Phenetylallylcarbamide, 154° ; *m*-phenetyl- β -chloropropylcarbamide, 116° ; *m*-phenetylpropylene- ψ -carbamide, $112\text{--}113^\circ$, *picrate*, $166\text{--}168^\circ$, *aurichloride*, 150° , *platinichloride*, 180° [$\text{R}=\text{C}_6\text{H}_4\cdot\text{OEt}$ (*m*)]. C. F. B.

Action of Phenylcarbimide on Ethyl β -Aminocrotonate. By ROBERT BEHREND and FERD. C. MEYER (*Ber.*, 1900, 33, 621—624).—Two compounds are formed by the action of phenylcarbimide on ethyl β -aminocrotonate.

1. *Ethyl β -phenyluraminocrotonate*, $\text{NHPh}\cdot\text{CO}\cdot\text{NH}\cdot\text{CMe}\cdot\text{CH}\cdot\text{CO}_2\text{Et}$, which is readily soluble in ether, but crystallises from light petroleum in broad, glistening needles melting at $98-99^\circ$. Its constitution follows from the fact that, on hydrolysis with alcoholic potash, it yields phenylmethyluracil.

2. An isomeric compound, $\text{NH}\cdot\text{CMe}\cdot\text{CH}(\text{CO}\cdot\text{NHPh})\cdot\text{CO}_2\text{Et}$, which is almost insoluble in ether; it crystallises from boiling alcohol in needles melting at $125-126^\circ$; on hydrolysis with alcoholic potash, it yields ammonia, carbon dioxide, aniline, and a compound melting at $83-84^\circ$, probably acetoacetanilide, and on treatment with concentrated sulphuric acid it yields ethyl acetylmalanilate (*Abstr.*, 1896, i, 593).

Phenylthiocarbimide and ethyl β -aminocrotonate yield a thick oil, together with crystals of *ethyl thiouraminocrotonate*, melting at 135° , which on hydrolysis yields *phenylthiomethyluracil*, melting at 255° . Methylthiocarbimide gives a product melting at $146-147^\circ$.

In a note BEHREND states that the two dimethyluracils (this vol., i, 120) are structurally isomeric, although they yield the same oxaluric acid, and he now agrees with Fischer's conclusion that δ -methyluric acid is 4-methyluric acid, not 6-methyluric as he formerly held (Behrend and Dietrich, this vol., i, 120). J. J. S.

Vinylideneoxanilide and its Homologues. By HANS VON PECHMANN and OTTO ANSEL (*Ber.*, 1900, 33, 613—621. Compare *Abstr.*, 1897, i, 135, 187).—The constitution, $\begin{matrix} \text{CO}\cdot\text{NPh} \\ \text{CO}\cdot\text{NPh} \end{matrix} > \text{C}\cdot\text{CH}_2$, as-

signed to vinylideneoxanilide is supported by the fact that only those fatty acids which contain at least one hydrogen atom attached to the α -carbon atom are capable of yielding similar derivatives with oxanilide. Vinylideneoxanilide is capable of undergoing two separate decompositions—an *anilide* decomposition into acetic acid and oxanilide or oxanilic acid and aniline, and an *amidine* decomposition into oxalic acid and vinylidenediphenyldiamine, which then becomes transformed into ethenyldiphenylamidine. The former hydrolysis is most readily brought about by the aid of alcoholic solutions of acids, or by ammonia and aniline; the latter hydrolysis by alcoholic potassium hydroxide, but the two may occur simultaneously. Vinylideneoxanilide is formed when the three dicarboxylic derivatives of oxanilide are heated with acetic anhydride and sodium acetate. Bromoethenyldiphenylamidine (*loc. cit.*) melts at 159° and not at 189° . *Ethylidene-*

oxanilide, $\begin{matrix} \text{CO}\cdot\text{NPh} \\ \text{CO}\cdot\text{NPh} \end{matrix} > \text{CHMe}$, formed when the vinylidene compound is reduced with zinc dust and alcohol in the presence of a little calcium chloride, crystallises from alcohol in glistening plates melting at $218-219^\circ$, and is readily soluble in most organic solvents; when warmed with alcoholic potash, it yields oxalic acid and Eibner's ethyldenediphenyldiamine. *Methyl oxanilide-m-dicarboxylate*, obtained by

heating methyl *m*-aminobenzoate and oxalic acid over the free flame, forms a crystalline powder melting at 236°, and when heated for 6—7 hours with sodium acetate and acetic anhydride, yields *methyl vinylideneoxanilide-m-dicarboxylate*, which crystallises in glistening needles melting at 194° and is sparingly soluble in alcohol or benzene.

Glyoxime-*N-p*-tolyl ether, sodium acetate, and acetic anhydride yield *vinylidene-p-oxalotoluidide*, $\begin{matrix} \text{CO}\cdot\text{N}(\text{C}_7\text{H}_7) \\ | \\ \text{CO}\cdot\text{N}(\text{C}_7\text{H}_7) \end{matrix} > \text{C}\cdot\text{CH}_2$, which crystallises from alcohol in glistening scales melting at 178°; when warmed with alcoholic potash, it yields *p*-ditolylethenylamidine melting at 121—121·5°, and, when reduced, *ethylidene-p-oxalotoluidide*, crystallising in long, glistening plates melting at 223°; when this is treated with alcoholic potash, it yields *ethylidene-p-ditolylidiamine*, $\text{CHMe}(\text{NH}\cdot\text{C}_7\text{H}_7)_2$, melting at 61°.

Bromovinylidene-β-oxalotoluidide, $\text{C}_8\text{N}_2\text{O}_2(\text{C}_7\text{H}_7)_2\cdot\text{CHBr}$, obtained by the action of bromine on a chloroform solution of vinylideneoxanilide, crystallises from alcohol in prisms which turn brown at 140° and melt at 160°; on treatment with alcoholic potash, it is converted into *p-ditolylbromoethenylamidine*, $\text{C}_7\text{H}_7\cdot\text{N}\cdot\text{C}(\text{CH}_2\text{Br})\cdot\text{NH}\cdot\text{C}_7\text{H}_7$, which crystallises in glistening plates melting at 148°.

Glyoxime-*N*-1 : 3 : 4-xylyl ether, sodium acetate, and acetic anhydride yield an *oxalylo-xylylidide* melting at 205°

Methylvinylideneoxanilide, $\begin{matrix} \text{CO}\cdot\text{NPh} \\ | \\ \text{CO}\cdot\text{NPh} \end{matrix} > \text{C}\cdot\text{CHMe}$, obtained from oxanilide, sodium propionate, and propionic anhydride, or, still better, from glyoxime-*N*-phenyl ether, separates from its hot chloroform solution, on the addition of light petroleum, as small prisms melting at 274—275°; on treatment with alcoholic potash, it yields diphenylpropenylamidine.

Dimethylvinylideneoxanilide, obtained from sodium isobutyrate, isobutyric anhydride, and oxanilide, forms glistening needles melting at 196—198°, and readily soluble in hot alcohol or chloroform. *Diphenylisobutenylamidine*, $\text{NPh}\cdot\text{CPr}^i\cdot\text{NHPh}$, crystallises in transparent prisms melting at 90—91°.

Dimethylethylacetic [α-dimethylbutyric] anhydride is a colourless liquid distilling at 227—228°, and does not react with oxanilide or glyoxime-*N*-phenyl ether. J. J. S.

4 : 1-Chloronaphthylamine. By FRÉDÉRIC REVERDIN and PIERRE CREPIEUX (*Ber.*, 1900, 33, 682—684).—The principal product of the chlorination of 1-acetylaminonaphthalene (compare Cleve, *Abstr.*, 1887, 494) by sodium chlorate and hydrochloric acid in acetic acid solution is 4 : 1-chloroacetylaminonaphthalene (m. p. 186·5°), which on hydrolysis yields 4 : 1-chloronaphthylamine melting at 98°; the latter is identical with Seidler's chloro-*α*-naphthylamine of undetermined constitution (*Abstr.*, 1878, 983), whilst Atterberg's 4 : 1-chloronaphthylamine, (*Ber.*, 1877, 10, 547) melting at 85—86°, is impure and after recrystallisation from light petroleum melts at 98°. W. A. D.

Constitution of Tribromophenol Bromide ("Tribromophenol brom"). By JOHANNES THIELE and HEINRICH EICHWEDE (*Ber.*, 1900, 33, 673—674).—Tribromophenol bromide is converted by lead acetate

at 60—70° in dilute acetic acid solution into 2:6-dibromoquinone. It must therefore have the formula $\text{CO} \begin{smallmatrix} \text{CBr}:\text{CH} \\ \text{CBr}:\text{CH} \end{smallmatrix} \text{CBr}_2$. Yet it does not form a semicarbazone; instead, it oxidises the semicarbazide, becoming itself reduced to tribromophenol. C. F. B.

Anethole and its Isomerides. By WILLIAM R. ORNDORFF and D. A. MORTON (*Amer. Chem. J.*, 1900, 23, 181—202. Compare Abstr., 1898, i, 129).—From the authors' previous work (*loc. cit.*), it seemed probable that anethole and liquid metanethole are stereoisomerides bearing the same relation to one another as fumaric and maleic acids. By a careful examination of their physical and chemical properties, and also of those of their derivatives, these two compounds are now shown to be identical.

By the action of alcoholic potash on anethole, an additive compound, $\text{C}_{10}\text{H}_{12}\text{O}, \text{C}_2\text{H}_6\text{O}$, is formed as a thin, colourless oil, lighter than water; it has a pleasant, mint-like odour, does not decolorise bromine, and when heated decomposes into anethole, alcohol, and solid metanethole.

Anethole hydrobromide, $\text{C}_{10}\text{H}_{12}\text{O}, \text{HBr}$, is a heavy oil resembling the hydrochloride.

On distilling anisoin, it decomposes into anethole and isoanethole, together with a small proportion of *p*-methoxytoluene.

An improved method for the preparation of anisoin is given.

T. H. P.

Action of Picryl Chloride on Catechol in Presence of Alkalis. By HOMER W. HILLYER (*Amer. Chem. J.*, 1900, 23, 125—128).—On warming a mixture of picryl chloride (1 mol.) and catechol (1 mol.) dissolved in alcohol containing sodium (2 at.) for 6 hours at 60—70°, sodium chloride and nitrite are formed, together with 3:5-dinitro-*o*-diphenylene oxide, $\text{C}_6\text{H}_4 \begin{smallmatrix} \text{O} \\ \diagup \quad \diagdown \\ \text{O} \end{smallmatrix} \text{C}_6\text{H}_2(\text{NO}_2)_2$; to indicate the analogy of this substance with dinitrophenoxazine (Turpin, *Trans.*, 1891, 69, 714), the name *dinitrophenoxozone* is proposed. It crystallises from glacial acetic acid in lemon-yellow, spherical aggregates, melts at 192—192·5°, and decomposes when rapidly heated, but sublimes in yellow leaflets when cautiously heated; it is indifferent towards dilute alkalis and hydrochloric acid, and dissolves unchanged in concentrated sulphuric acid, being precipitated on dilution.

W. A. D.

Preparation of Resorcinol Monomethyl Ether. By VICTOR MERZ and H. STRASSER (*J. pr. Chem.*, 1900, [ii], 61, 109—113).—In preparing resorcinol monomethyl ether by heating resorcinol with potassium hydrogen sulphate and methyl alcohol (Wallach and Wüsten, *Abstr.*, 1883, 1096), the yield amounted in three experiments to 30, 33, and 35 per cent. of the theoretical. T. M. L.

Eugenol, Safrole, and Propylcatechol. By RAYMOND DELANGE (*Compt. rend.*, 1900, 130, 659—660).—*Propylcatechol*, $\text{C}_6\text{H}_3\text{Pr}(\text{OH})_2$ [Pr:OH:OH = 1:3:4], is obtained (1) by methylating eugenol, boiling the resulting allylveratrole with alcoholic potash to convert it into the

isomeric propenylveratrole, reducing the latter by means of sodium and boiling alcohol, and treating the propylveratrole thus obtained with hydriodic acid; (2) by boiling safrole with alcoholic potash, reducing the isosafrole thus formed to propylmethylenecatechol, treating the latter with phosphorus pentachloride, and decomposing the dichloride produced with water. Propylcatechol is a white, crystalline compound of faint, agreeable odour; it melts at 60° , boils at $175\text{--}180^{\circ}$ under 30 mm. pressure, and is slightly soluble in water and very soluble in most organic solvents. The aqueous solution reduces ammoniacal silver nitrate in the cold, and yields a greenish-blue coloration with ferric chloride, which is changed to wine-red by the addition of sodium carbonate.

N. L.

Nitroso-derivatives of the Phloroglucinol Ethers. By HUGO WEIDEL and JACQUES POLLAK (*Monatsh.*, 1900, 21, 15—35. Compare Abstr., 1898, i, 15).—*Phloroglucinol monomethyl ether*, prepared by the etherification of phloroglucinol at low temperatures, boils at 213° under 16 mm. pressure, and solidifies to a yellowish mass of crystals, which melts at $75\text{--}78^{\circ}$; by the authors' method of treatment (*loc. cit.*), it yields a diisonitroso-derivative, probably $\text{OMe} \begin{smallmatrix} \text{C}(\text{N}\cdot\text{OH})\cdot\text{CO} \\ \text{CH} \text{---} \text{CO} \end{smallmatrix} \text{C}\cdot\text{N}\cdot\text{OH}$,

which forms a reddish-yellow mass of crystals melting at about 150° , gives a characteristic monopotassium derivative, and on reduction with stannous chloride and hydrochloric acid, yields 2:4-diamino-3:5-dihydroxyanisole hydrochloride, which decomposes on exposure to the air, but forms a well-characterised tetra-acetyl derivative melting at 169° .

When phloroglucinol dimethyl ether is treated with a nitrite and acetic acid, the greater part is converted into 3:5-dimethoxy-o-quinone-2-monoxime, small quantities of 3:5-dimethoxy-p-quinone-2-monoxime being formed at the same time. 3:5-Dimethoxy-o-quinone-2-monoxime crystallises from alcohol in dark red, lustrous leaflets melting at $175\text{--}176^{\circ}$, and on reduction with stannous chloride and hydrochloric acid yields 2-amino-3:5-dimethoxyphenol hydrochloride, which forms reddish needles melting at $205\text{--}206^{\circ}$, and on fusion with carbamide, yields

3:5-dimethoxycarbonyl-2-aminophenol, $\text{CO} \begin{smallmatrix} \text{NH}\cdot\text{C}\cdot\text{C}(\text{OMe})\cdot\text{CH} \\ \text{O} \text{---} \text{C} \text{---} \text{CH} \text{---} \text{C}\cdot\text{OEt} \end{smallmatrix}$, which crystallises in needles melting at $210\text{--}211^{\circ}$.

3:5-Dimethoxy-p-quinone-4-monoxime forms long, yellow needles, which become coloured at 185° and melt at 222° ; on reduction, it yields 4-amino-3:5-dimethoxyphenol hydrochloride, which crystallises from dilute hydrochloric acid, with H_2O , in snow-white, silky needles melting and decomposing at $171\text{--}173^{\circ}$, and is oxidised by ferric chloride to 3:5-dimethoxyquinone, thus affording a proof of the constitution of the p-quinonemonoxime. The 4-amino-3:5-diethoxyphenol hydrochloride previously described (*loc. cit.*) yields, on treatment with ferric chloride, an analogous 3:5-diethoxyquinone, which crystallises from chloroform in yellow needles melting at $118\text{--}122^{\circ}$, and gives a characteristic red coloration with concentrated sulphuric acid.

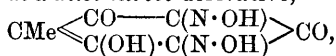
R. H. P.

Ethylphloroglucinol and other Derivatives of Ethylbenzene. By GUSTAV WEISWEILLER (*Monatsh.*, 1900, 21, 39—49).—2 : 4-Dinitro-1-ethylbenzene, prepared by the action, at 125—130°, of a mixture of 1 part of nitric acid, of sp. gr. 1.43, and 2 parts of sulphuric acid on ethylbenzene, is a viscous, yellow oil which boils at 167.5° under 13 mm. pressure; when reduced by tin and hydrochloric acid, it yields 2 : 4-diamino-1-ethylbenzene dihydrochloride, which is colourless when crystallised from alcohol, but becomes dark red on contact with water; the diacetyl derivative of the corresponding base is formed when the dihydrochloride is treated with acetic anhydride, and crystallises in slender needles melting at 224°; the monoacetyl derivative formed in small quantities at the same time melts at 319—320°.

s-Trinitroethylbenzene is prepared by the action of a mixture of 1 part of nitric acid, of sp. gr. 1.525, and 4 parts of fuming sulphuric acid ($\text{SO}_3 : 2\text{H}_2\text{SO}_4$) on ethylbenzene; it is separated from the dinitro-derivative by means of the additive compound with aniline, $\text{C}_6\text{H}_5\text{Et}(\text{NO}_2)_3 + \text{NH}_2\text{Ph}$, which is precipitated by light petroleum from a benzene solution of aniline and the crude nitration product in red needles melting at 44—45°. This additive compound is decomposed by acids into an aniline salt and *s*-trinitroethylbenzene, which crystallises from alcohol in yellow leaflets melting at 37°; on reduction with tin and hydrochloric acid, it yields diaminohydroxyethylbenzene dihydrochloride, which yields a triacetyl derivative of the base, forming small, white needles melting at 259—262°. When the dihydrochloride is treated with a large excess of water, it is converted into ethylphloroglucinol, $\text{C}_6\text{H}_5\text{Et}(\text{OH})_3$, which boils at 209—210° under 12 mm. pressure, and solidifies to a mass of white crystals melting at 119—120°; it yields a liquid triacetyl derivative, which boils at 208—209° under 15.8 mm. pressure.

R. H. P.

Action of Nitrous Acid on Methylphloroglucinol. By HUGO WEIDEL and JACQUES POLLAK (*Monatsh.*, 1900, 21, 50—61. Compare preceding page).—Methylphloroglucinol, on treatment with a nitrite and acetic acid, yields a diisonitroso-derivative,



which crystallises from water, with H_2O , in bright, yellow needles melting at 154—155°, and forms a characteristic copper-red potassium salt; on reduction, this gives the very unstable 3 : 5-diamino-2 : 4 : 6-trihydroxytoluene hydrochloride, which is characterised by the penta-acetyl derivative, crystallising in needles and melting at 217—218°. During the preparation of this acetyl derivative, a compound of undetermined composition is obtained, which forms lustrous tablets melting at 114°. When the diisonitroso-compound is treated with hydroxylamine and alcohol, a monoxime is obtained, which melts at 189—190°, and, on reduction with tin and hydrochloric acid, yields a triaminodihydroxytoluene dihydrochloride. The constitutions of this oxime and of its reduction product have not yet been determined.

R. H. P.

Preparation of Dimethyl-1 : 2 : 3 : 5-phentetrol. By HEINRICH BRUNNMAYR (*Monatsh.*, 1900, 21, 1—14).—Nitrosodimethylphloroglucinol is easily obtained by treating dimethylphloroglucinol at -5°

with nitric acid, which has been saturated with nitrous acid; it crystallises in orange-red tablets melting at 158° , and colours concentrated hydrochloric acid an intense violet, but does not give Liebermann's reaction; it is easily reduced by stannous chloride, yielding *amino-dimethylphloroglucinol hydrochloride*, which crystallises with H_2O in colourless needles, and on treatment with acetic anhydride yields a *penta-acetyl* derivative, which crystallises in small, lustrous cubes melting at 169° . *Dihydroxy-m-xyloquinone*, obtained by the oxidation of the hydrochloride just mentioned with ferric chloride, crystallises in deep red, lustrous leaflets, which melt and sublime at 167° ; it is strongly acidic, dissolving in alkaline liquids giving a deep blue-violet coloration. On reduction by stannous chloride in acid solution, it yields *dimethyl-1:2:3:5-phentetrol*, which crystallises from light petroleum in pale rose-coloured needles melting at 189° , gives similar colour reactions to those described by Oettinger (Abstr., 1895, i, 457) for 1:2:3:5-phentetrol, and yields a *tetra-acetyl* derivative which crystallises in colourless, transparent needles melting at 154° . R. H. P.

ψ -Phenylacetic Acid. By WILHELM BRAREN and EDUARD BUCHNER (*Ber.*, 1900, 33, 684—691. Compare Abstr., 1898, i, 639—640).—On reducing bromocycloheptenecarboxylic acid (*loc. cit.*) with zinc dust and acetic acid, Δ^1 -cycloheptenecarboxylic acid (suberenecarboxylic acid), melting at 51 — 52° , is formed, together apparently with a smaller proportion of the isomeric Δ^2 -acid, although the latter could not be isolated. β -Isophenylacetic acid, on reduction with sodium amalgam at the ordinary temperature, gives rise to Δ^2 -cycloheptenecarboxylic acid, which melts at 18 — 20° , boils at 250 — 253° under 735 mm. pressure, and is identical with the so-called Γ - Δ^2 -1:4-ethylcyclopentenecarboxylic acid obtained by Einhorn and Willstätter (Abstr., 1894, i, 523) on reducing *p*-methylenedihydrobenzoic acid (Abstr., 1893, i, 378); the amides of both acids are also identical. When Δ^2 -cycloheptenecarboxylic acid is heated with alcoholic potassium hydroxide, it undergoes rearrangement into the foregoing Δ^1 -acid.

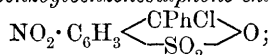
Bromocycloheptenecarboxylic acid readily unites with bromine at the ordinary temperature in glacial acetic acid solution to form *tribromocycloheptanecarboxylic acid*, which crystallises from formic acid, melts at 161 — 162° , and is stable towards aqueous potassium permanganate.

In a supplementary note, E. BUCHNER deals very fully with Willstätter's contention (Abstr., 1899, i, 651) that the amide of Δ^1 -cycloheptenecarboxylic acid melts at 134 — 135° ; it is maintained that the true melting point is 126° . W. A. D.

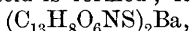
Symmetrical *p*-Nitro-*o*-sulphobenzoic Chloride. By FRED S. HOLLIS (*Amer. Chem. J.*, 1900, 23, 233—255).—By heating potassium hydrogen *p*-nitro-*o*-sulphobenzoate (1 mol.) with phosphorus pentachloride (2.5 mols.) at 150° for 5 hours, the unsymmetrical dichloride of the acid is alone formed (compare Remsen and Gray, Abstr., 1897, i, 477).

The action of benzene and aluminium chloride on either the sym-

metrical or the unsymmetrical dichloride of *p*-nitro-*o*-sulphobenzoic acid gives rise to *p*-nitro-*o*-benzoylbenzenesulphonate chloride,



it separates from benzene on adding ether in the form of small, purple, or green, apparently monoclinic crystals, having a rhombohedral habit, and melts at 177°. By the action of either hydrochloric acid, sulphuric acid, water, or alcohol on the sulphonic chloride, *p*-nitro-*o*-benzoylbenzenesulphonic acid is formed; its *barium* salt,



forms monoclinic crystals containing varying amounts of water of crystallisation and has an intensely bitter taste; the *sodium* (with H_2O), *potassium*, *magnesium* (with $9\frac{1}{2}\text{H}_2\text{O}$), *calcium* (with $3\text{H}_2\text{O}$), and *lead* (with $5\frac{1}{2}\text{H}_2\text{O}$) salts are described.

On heating phosphorus pentachloride and sodium *p*-nitro-*o*-benzoylbenzenesulphonate together, the corresponding sulphonic chloride, just described, is obtained.

The action of ammonia on *p*-nitro-*o*-benzoylbenzenesulphonic chloride gives rise firstly to the *lactim* of *p*-nitro-*o*-benzoylbenzenesulphonic acid, $\text{NO}_2 \cdot \text{C}_6\text{H}_3 \begin{array}{c} \text{CPh} \\ \diagup \quad \diagdown \\ \text{SO}_2 \end{array} \text{N}$, which is a pale green, granular powder melting at 234°; it dissolves readily in benzene, but only slightly in alcohol, and by the continued action of ammonia suffers decomposition. Concentrated hydrochloric acid at a high temperature converts the lactim into *ammonium p*-nitro-*o*-benzoylbenzenesulphonate, which forms either a yellow, crystalline powder or thick, acicular crystals; it dissolves readily in water and gives no definite melting point. T. H. P.

Rearrangement of Imino-ethers. II. By HENRY L. WHEELER (*Amer. Chem. J.*, 1900, 23, 135—150. Compare Wheeler and Johnson, *Abstr.*, 1899, i, 431).—Methyl iodide acts on benziminomethyl ether at the ordinary temperature in the same manner as at 100°, benzomethylamide being formed along with benzamide, benzonitrile, and a trace of cyanphenin; the proportion of methyl iodide used has no influence on the result. Similar results were obtained with ethyl iodide and benziminoethyl ether (compare *loc. cit.*); in this action, no benzodiethylamide is formed. On heating benziminoisobutyl ether with methyl iodide for 4 hours at 80—115°, isobutyl iodide and benzomethylamide are formed, together with a smaller proportion of benzamide and cyanphenin; benzomethylamide melts at 82°, not at 78° as stated by Romburgh (*Rec. Trav. Chim.*, 1886, 4, 387). When benziminoisobutyl ether is heated at 165—185° for several hours with isobutyl iodide, the latter is decomposed into isobutylene and hydrogen iodide, which converts the imino-ether into benzamide with regeneration of isobutyl iodide; *benzoisobutylamide*, prepared from isobutylamine by the Baumann-Schotten reaction, crystallises from alcohol in chisel-shaped prisms, melts at 57—58°, and boils at 173—178° under 13 mm. pressure, and with partial decomposition at 308—313° under 760 mm. pressure. Benziminoethyl ether and isobutyl iodide yield benzamide, benzonitrile, cyanphenin, benzethylamide, benzoisobutyl-

amide, and a small quantity of a *substance* separating from alcohol in colourless crystals and melting with effervescence at 192° .

[With TREAT B. JOHNSON.]—Phenylacetiminomethyl ether and methyl iodide, when heated together at $95\text{--}105^{\circ}$, yield phenylacetamide, phenylacetonitrile, and phenylacetomethylamide; quantitative experiments show that neither the amount of methyl iodide used nor the time of heating influences the relative proportions of the products formed. Phenylacetiminoethyl ether and ethyl iodide in a similar manner give phenylacetomethylamide.

[With MUNSON D. ATWATER.]—*Furfuriminomethyl ether*,
 $\text{OMe}\cdot\text{C}(\text{C}_4\text{OH}_3):\text{NH}$,

prepared from furfuryl cyanide by Pinner's method, is a colourless oil with a characteristic odour which boils at $52\text{--}57^{\circ}$ under 8 mm. and at $169\text{--}172^{\circ}$ under 762 mm. pressure; with methyl iodide, either at the ordinary temperature or at 100° , it yields a small quantity of pyromucamide, together with a larger proportion of *pyromucomethylamide*, $\text{C}_6\text{H}_7\text{O}_2\text{N}$, which crystallises from light petroleum and forms stout, colourless crystals, melts at 64° , and boils at $250\text{--}253^{\circ}$ under the ordinary pressure.

p-Tolonyliminomethyl ether, prepared from *p*-toluonitrile by Pinner's method, boils at 105.5° under 10.5 mm. pressure; with methyl iodide, it yields *p*-toluomethylamide [m. p. $144\text{--}145^{\circ}$; Gattermann and Schmidt (*Annalen*, 1887, 244, 51) give 143°]. When heated with methyl alcohol at $100\text{--}140^{\circ}$ for 6 hours and finally at $150\text{--}175^{\circ}$, it yields *p*-toluonitrile and a small quantity of *p*-toluamide, no molecular rearrangement occurring.

β -Naphthyliminoethyl ether, prepared from *β* -naphthonitrile, when heated with ethyl iodide, yields only a small proportion of *β* -naphthoethylamide (m. p. $129\text{--}131^{\circ}$).

[With BAYARD BARNES.]—Although silver succinimide yields oxygen-ethers with alkyl iodides at the ordinary temperature (Comstock and Wheeler, Abstr., 1892, 701), nitrogen-ethers are obtained at higher temperatures owing to rearrangement occurring; methyl iodide at 100° yields succinomethylimide, and ethyl iodide during 12 hours at 100° , succinoethylimide, together with a certain proportion of the oxygen-ether, characterised by the compound it forms with aniline (*loc. cit.*).

Benzoylbenziminomethyl ether, $\text{OEt}\cdot\text{CPh}\cdot\text{NBz}$, when heated with ethyl iodide for 8 hours at $110\text{--}120^{\circ}$, does not undergo rearrangement, but is decomposed into benzonitrile and ethyl benzoate.

W. A. D.

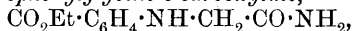
Decomposition of Benzenylmethyliminochloride. By HANS VON PECHMANN [with JULIUS OBERMILLER] (*Ber.*, 1900, 33, 611—612. Compare Abstr., 1896, i, 31).—The compound previously obtained by distilling benzenylmethyliminochloride under diminished pressure is now shown to be cyanphenin. When the same iminochloride is boiled for some time, or is distilled several times, under atmospheric pressure, it is decomposed into methyl chloride and benzonitrile.

From Wallach's researches, it follows that aromatic substituted

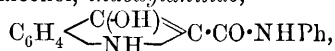
iminochlorides of aromatic acids can be distilled without undergoing decomposition, whereas aromatic and aliphatic derivatives of iminochlorides of aliphatic acids are readily decomposed. The authors think it probable that aliphatic substituted iminochlorides of aromatic acids are readily decomposed into alkyl chlorides and aromatic nitriles or their polymerides. J. J. S.

Isomeric Mono-esters of Phenylglycine-*o*-carboxylic Acid. By DANIEL VORLÄNDER and RUDOLF VON SCHILLING (*Ber.*, 1900, 33, 553—554).—Mono-esters of phenylglycinecarboxylic acid of the constitution $\text{CO}_2\text{H}\cdot\text{C}_6\text{H}_4\cdot\text{NH}\cdot\text{CH}_2\cdot\text{CO}_2\text{R}$ are obtained by the direct esterification of the acid, or by heating anthranilic acid with the esters of monochloroacetic acid. The *methyl* ester melts at 160° , and the *ethyl* ester at 152° . The isomeric mono-esters are obtained by the partial hydrolysis of the di-esters. Both the *methyl* and *ethyl* esters melt somewhat indefinitely at about 182° , after first softening. A. H.

Action of Ammonia and Aniline on Phenylglycine-*o*-carboxylic Acid. By DANIEL VORLÄNDER and H. WEISSBRENNER (*Ber.*, 1900, 33, 555—556).—Ammonia and aniline react chiefly with the aliphatic carboxyl group of phenylglycine-*o*-carboxylic acid, or its esters. *Ethyl aminophenylglycine-*o* carboxylate*,



crystallises in white needles melting at 180 — 182° . The *diamide* forms narrow plates melting at 198 — 200° . *Anilinophenylglycine-*o*-carboxylic acid*, $\text{CO}_2\text{H}\cdot\text{C}_6\text{H}_4\cdot\text{NH}\cdot\text{CH}_2\cdot\text{CO}\cdot\text{NHPh}$, crystallises in white needles and melts and decomposes at 235° ; the corresponding *methyl* ester melts at 140 — 142° , and the *ethyl* ester at 164 — 166° . When the methyl or ethyl ester of the anilino compound is treated with sodium ethoxide free from alcohol, *indoxylanilide*,



is produced; it crystallises in colourless needles, and decomposes gradually when slowly heated; when rapidly heated, indigotin is formed. A. H.

Acetylation of Phenylglycine-*o*-carboxylic Acid. By DANIEL VORLÄNDER and H. WEISSBRENNER (*Ber.*, 1900, 33, 556—557).—*Diethyl acetylphenylglycine-*o*-carboxylate*, $\text{CO}_2\text{Et}\cdot\text{C}_6\text{H}_4\cdot\text{NAc}\cdot\text{CH}_2\cdot\text{CO}_2\text{Et}$, obtained by the action of acetic anhydride or acetyl chloride on diethylphenylglycine-*o*-carboxylate, crystallises in large, colourless tablets and melts at 61° . By sulphuric acid, containing more than 99.1 per cent. of acid, it is converted at 100° into indigotinsulphonic acid, whilst a weaker acid does not produce indigotin. Indigotin is also produced when the compound is boiled with 20 per cent. aqueous potash and the solution exposed to the air. Acetylphenylglycine-*o*-carboxylic acid forms white crystals, which melt and decompose at about 210° . This acid is identical with that prepared from acetyl-*o*-tolylglycine (German Patent 102893). It is readily converted into indigotin by strong sulphuric acid, but not by alkalis. A. H.

Benzenestearosulphonic [Sulphophenylstearic] Acid and other Sulphonic Acids containing the Stearyl Group. By ERNST TWITCHELL (*J. Amer. Chem. Soc.*, 1900, 22, 22—26).—*Sulphophenylstearic acid*, $\text{SO}_3\text{H}\cdot\text{C}_6\text{H}_4\cdot\text{C}_{18}\text{H}_{35}\text{O}_2$, is formed when a mixture of benzene and oleic acid is treated with an excess of sulphuric acid, care being taken to avoid any excessive rise in temperature. When dried at 100° , it forms a very viscous oil which, on cooling, sets to a semi-solid mass. The acid and both its normal and acid alkali salts are soluble in water, yielding colloidal solutions, and are precipitated by the addition of an acid, alkali, or salt. The acid is only slowly decomposed by heating at 170° with hydrochloric acid, and when fused with potash it gives potassium sulphite.

Sulphonaphthylstearic Acid, $\text{SO}_3\text{H}\cdot\text{C}_{10}\text{H}_6\cdot\text{C}_{18}\text{H}_{35}\text{O}_2$, is rather less fluid than the benzene compound; *sulphophenolstearic acid* has not been obtained in a pure form. J. J. S.

Constitution of Chrysenic Acid. By CARL GRAEBE (*Ber.*, 1900, 33, 680—681).—In the preparation of chrysenic acid, according to Bamberger and Burgdorf's method (*Abstr.*, 1890, 1312), by fusing chrysoquinone with a caustic alkali, a better yield is obtained when lead dioxide is added. Besides the chrysenic acid melting at 190° (corr.), an isomeride, melting at 114° and more soluble, is obtained; this is named β -chrysenic acid. Both acids also result from the action

of caustic alkali on chrysoketone, $\text{C}_{10}\text{H}_6 > \text{CO}$. Of the two possible formulæ, that in which the two ortho-positions relatively to the

carboxyl are substituted, $\text{CH}:\text{CH}:\text{C}:\text{CH}=\text{CH}$
 $\text{CH}:\text{CH}:\text{C}:\text{C}(\text{CO}_2\text{H})\cdot\text{C}\cdot\text{C}_6\text{H}_5$, must be as-

signed to β -chrysenic acid, which does not yield an ester when treated with methyl alcohol and sodium chloride at the ordinary temperature, whilst to chrysenic acid, which does form an ester, the other formula, $\text{CH}:\text{CH}:\text{C}\cdot\text{C}_{10}\text{H}_7$
 $\text{CH}:\text{CH}:\text{C}\cdot\text{CO}_2\text{H}$, must be given. C. F. B.

Preparation of Naphthalic Acid. By GEORGE F. JAUBERT (*Ber.*, 1900, 33, 649).—A reply to Anselm and Zuckmayer (this vol., i, 175). T. H. P.

3:4-Dichloro-2-dimethylaminobenzoylbenzoic Acid. By ÉMILE SEVERIN (*Compt. rend.*, 1900, 130, 723—725).—3:4-Dichloro-2-dimethylaminobenzoylbenzoic acid, $\text{NMe}_2\cdot\text{C}_6\text{H}_4\cdot\text{CO}\cdot\text{C}_6\text{H}_2\text{Cl}_2\cdot\text{CO}_2\text{H}$, prepared by Haller and Guyot's method (*Abstr.*, 1894, i, 602) from 3:4-dichlorophthalic anhydride and dimethylaniline, crystallises from alcohol in yellow flakes melting at 222° . The acetate (mixed anhydride), $\text{NMe}_2\cdot\text{C}_{13}\text{H}_6\text{OCl}_2\cdot\text{CO}\cdot\text{OAc}$, formed by heating it with acetic anhydride on the water-bath for 2 hours, crystallises from hot benzene or alcohol in colourless leaflets and melts at 170° .

The methyl ester of the above acid, produced by treating the preceding compound with the theoretical quantity of sodium methoxide, forms highly refractive crystals melting at 160° ; it cannot be obtained from its acid by the ordinary methods of esterification, the latter substance belonging to the category of ortho-disubstituted acids studied by V. Meyer.

The *ethyl* ester crystallises in colourless needles and melts at 156°.

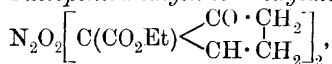
The *nitroso*-compound, $\text{NMe}_2 \cdot \text{C}_6\text{H}_3(\text{NO}) \cdot \text{CO} \cdot \text{C}_6\text{H}_2\text{Cl}_2 \cdot \text{CO}_2\text{H}$, formed by the action of sodium nitrite on the acid dissolved in acetic acid, crystallises from methyl alcohol in yellow needles containing 1 mol. of the solvent, and melts at 165°.

G. T. M.

Nitroso-compounds derived from Cyclic 2-Ketocarboxylic Esters (Bisnitroso-2-ketocarboxylic Esters and α -Oximinodicarboxylic Acids). By WILHELM DIECKMANN (*Ber.*, 1900, 33, 579—595).—The cyclic 2-ketocarboxylic esters, on treatment with ethyl nitrite and sodium ethoxide, yield the corresponding α -oximinodicarboxylic acids, which are decomposed by heat, with formation of the half-nitrile of the next lower homologue; when, however, ethyl nitrite and hydrochloric acid or acetyl chloride are used, the 2-ketocarboxylic esters are partly converted into bisnitroso-2-ketocarboxylic esters, a class of compounds which are very similar to the bisnitroso-compounds of the terpene series (von Baeyer, *Abstr.*, 1895, i, 379), and on treatment with alcoholic potash are easily converted into the α -oximinodicarboxylic acids.

Ethyl α -oximinoadipate, obtained from ethyl 2-ketopentamethylenecarboxylate, forms colourless needles melting at 52—53°, and on hydrolysis yields *α -oximinoadipic acid*, $\text{CO}_2\text{H} \cdot \text{C}(\text{N} \cdot \text{OH}) \cdot [\text{CH}_2]_3 \cdot \text{CO}_2\text{H}$, which forms small, white crystals melting at 151—152°, yields a characteristic *silver hydrogen* salt, and when heated above its melting point decomposes with the formation of *γ -cyanobutyric acid*, which crystallises in very hygroscopic, colourless tablets melting at about 45°.

Diethyl bisnitroso-2-ketopentamethylenecarboxylate,

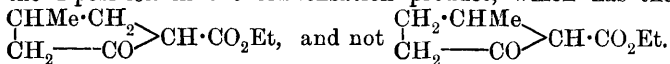


obtained from ethyl 2-ketopentamethylenecarboxylate, forms colourless crystals, which on warming turn green, then melt, and decompose at 114°.

α -Oximinopimelic acid, $\text{CO}_2\text{H} \cdot \text{C}(\text{N} \cdot \text{OH}) \cdot [\text{CH}_2]_4 \cdot \text{CO}_2\text{H}$, obtained from ethyl 2-ketohexamethylenecarboxylate, melts at 142—143°, forms a crystalline *silver hydrogen* salt, and when heated gives an oil which, on hydrolysis, yields adipic acid. *Diethyl bisnitroso-2-ketohexamethylenecarboxylate* forms colourless crystals, which on warming turn green, melt, and decompose at 110°.

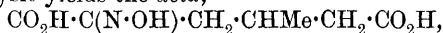
R. H. P.

Nitroso-compounds from Ethyl Methyl-2-ketopentamethylenecarboxylate, obtained by the Condensation of Ethyl β -Methyladipate, and their Constitution. By WILHELM DIECKMANN and A. GROENEVELD (*Ber.*, 1900, 33, 595—605. Compare preceding abstract).—Ethyl methyl-2-ketopentamethylenecarboxylate, obtained by the condensation of ethyl β -methyladipate, can be converted into ethyl α -oximino- γ -methyladipate, which in turn can be converted into β -methylglutaric acid, thus showing that the methyl group occupies the 4-position in the condensation product, which has the formula



Ethyl α -oximino- β -methyladipate, obtained by treating ethyl 4-methyl-

2-ketopentamethylenecarboxylate with nitrous acid, melts at 59—60° and on hydrolysis yields the *acid*,



which forms colourless crystals melting at 162—163°, yields a characteristic *silver hydrogen* salt, and by successive treatment with acetic anhydride and potash yields β -methylglutaric acid.

Ethyl bisnitroso-4-methyl-2-ketopentamethylenecarboxylate crystallises in colourless, prismatic needles melting and decomposing at 94°; the corresponding *methyl* ester is very similar and has the same melting point, both yield on hydrolysis α -oximino- γ -methyladipic acid.

R. H. P.

Acetals from Phenols. By R. FOSSE (*Compt. rend.*, 1900, 130, 725—727. Compare Claisen, *Abstr.*, 1887, 270; Moureu, *Abstr.*, 1898, i, 660; 1899, i, 30, 493 and 679).—as *Diphenoxyethane*, obtained by heating at 120° a dilute alcoholic solution of phenol, ethylidene chloride, and potassium hydroxide and distilling the product under diminished pressure, crystallises from liquid methyl chloride and melts at 10°; at the ordinary temperature, it is an amber-coloured oil having an aromatic odour; it boils at 174—176° under 27 mm. pressure and can be distilled in steam.

as *Dinaphthoxyethane*, prepared in a similar manner, crystallises from alcohol in colourless needles melting at 117°.

When heated with dilute sulphuric acid, these aromatic acetals are readily hydrolysed into acetaldehyde and the corresponding phenol.

G. T. M.

Ketone Reactions of Cyclopentadiene. By JOHANNES THIELE (*Ber.*, 1900, 33, 666—673).—The hydrogen atom in the grouping $\text{CH}\cdot\text{C}:\text{C}$ has not the same replaceability as in $\text{CH}:\text{C}:\text{O}$; in $\text{CH}_2(\text{C}:\text{C})_2$, however, the replaceability is at last equal to that in ketones, as is

exemplified by cyclopentadiene, $\text{CH}_2\begin{smallmatrix} \text{CH}:\text{CH} \\ \diagup \quad \diagdown \\ \text{CH}:\text{CH} \end{smallmatrix}$. When a mixture of

this substance (Kramer and Spilker, *Abstr.*, 1896, i, 289) with ethyl nitrite is added gradually to alcoholic sodium ethoxide at 20—30°,

bisisonitrosocyclopentadiene, $(\text{OH}\cdot\text{N}:\text{C}\begin{smallmatrix} \text{CH}:\text{CH} \\ \diagup \quad \diagdown \\ \text{CH}:\text{CH} \end{smallmatrix})_2$, is formed; it melts

and decomposes at 185—186°, and yields a *benzoyl* derivative, $(\text{C}_5\text{H}_4\text{ONBz})_2$, which melts and decomposes at 208—209°. When ethyl nitrate is used instead of the nitrite, at the ordinary temperature,

nitrocyclopentadiene, $\text{NO}_2\cdot\text{CH}\begin{smallmatrix} \text{CH}:\text{CH} \\ \diagup \quad \diagdown \\ \text{CH}:\text{CH} \end{smallmatrix}$, is formed; this substance is

very unstable, but its *sodium* and *silver* derivatives were prepared and analysed; with an alkali diazobenzenesulphonate, it forms a colouring matter. Cyclopentadiene also condenses with ethyl oxalate in the presence of lukewarm alcoholic sodium ethoxide; *ethyl cyclopentadieneoxalate*, $\text{CO}_2\text{Et}\cdot\text{CO}\cdot\text{CH}\begin{smallmatrix} \text{CH}:\text{CH} \\ \diagup \quad \diagdown \\ \text{CH}:\text{CH} \end{smallmatrix}$, was isolated in the form

of its red sodium derivative, which could not be obtained pure, however; with an alkali diazobenzenesulphonate, it forms a dye. Cyclopentadiene also condenses with acetone, acetophenone, or benzophenone

in the presence of sodium ethoxide; the first product boils at 46° under 11 mm., $153\text{--}154^\circ$ under 717 mm. pressure and has a sp. gr. 0.8858 at $17^\circ/4^\circ$; the second boils at 130.5° under 10.5 mm.; the third melts at 82° ; they are coloured orange to red, and are more or less unstable in the air. They are named *dimethylfulvene*, *phenylmethylfulvene*, and *diphenylfulvene*, being regarded as derivatives of a hydro-

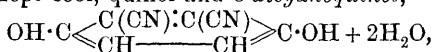
carbon, $\text{CH}_2\text{:C} \begin{smallmatrix} \text{CH:CH} \\ \text{CH:CH} \end{smallmatrix}$, which is named fulvene because its deriva-

tives are coloured. Evidently the carbon nucleus which it contains is chromophoric in character; it is pointed out that similar nuclei exist in other coloured substances, for example, in quinone and phorone. Cyclopentadiene also condenses with aldehydes to form coloured products, but these are very unstable; *phenylfulvene* is dark red and melts at about 31° ; with formaldehyde, which theoretically should yield fulvene itself, no well-defined product could be obtained. With diazobenzene chloride in alkaline solution cyclopentadiene yields a coloured product, but here, again, no well-defined substance could be isolated. C. F. B.

Solubility of Benzophenone. By E. DERRIEN (*Compt. rend.*, 1900, 130, 721—723).—Determinations of the solubility of benzophenone in thirty-two organic and inorganic solvents are recorded.

G. T. M.

Addition of Hydrogen Cyanide to Quinone. By JOHANNES THIELE and J. MEISENHEIMER (*Ber.*, 1900, 33, 675—676).—When a strong solution of potassium cyanide is added gradually to an alcoholic solution of quinone which contains sulphuric acid in addition, the solution being kept cool, quinol and *o*-dicyanoquinol,



are formed, the latter in yield greater than 70 per cent. This substance is yellowish, and blackens at about 230° when anhydrous; it is stable with aqueous acids and alkalis, but when warmed for $\frac{1}{4}$ hour on the water-bath with concentrated sulphuric acid, is converted to the extent of about 90 per cent. into *p*-dihydroxyphthalimide,

$\text{C}_6\text{H}_2(\text{OH})_2 \begin{smallmatrix} \text{CO} \\ \text{CO} \end{smallmatrix} \text{NH} + 3\text{H}_2\text{O}$, which is yellow, does not melt below 240° , and yields *p*-dihydroxybenzoic acid when boiled for several hours with strong hydrochloric acid. Both substances give fluorescent solutions. C. F. B.

Action of Nitrogen Trioxide on α -Naphthaquinone. By JULIUS SCHMIDT (*Ber.*, 1900, 33, 543—547).— α -Naphthaquinone dissolves in liquid nitrogen trioxide (prepared from arsenious anhydride and nitric acid), and after several days thick, dark red crystals of

1:3-diketohydrindene nitrosite, $\text{C}_8\text{H}_4 \begin{smallmatrix} \text{CO} \\ \text{CO} \end{smallmatrix} \text{C}\cdot\text{N}_2\text{O}_3$, separate; this melts and decomposes at 160° , gives Liebermann's nitroso-reaction, dissolves in alkalis with a deep red coloration, and slowly decomposes on keeping, with evolution of nitrous fumes. Water at the ordinary temperature converts it into 1:3-diketohydrindene, together with

anhydrobisdiketohydrindene (Wislicenus, Abstr., 1887, 587; with Kotzle, *ibid.*, 1889, 1067; with Reitzenstein, Abstr., 1894, i, 133); the latter alone is formed by the action of water at 100°, whilst when the dry nitrosite is heated, phthalic anhydride is obtained.

W. A. D.

Spontaneous Oxidation, "Autoxidation," and Formation of Active Oxygen ("Sauerstoffaktivierung"). By WILHELM MANCHOT (*Chem. Centr.*, 1900, i, 132—133; from *Habilitationschrift*, Göttingen, 1899).—The products formed by the direct action of oxygen on derivatives of anthracene, phenanthrene, and similar hydrocarbons are much less complex and more easily isolated than those similarly obtained from benzene derivatives. By the action of atmospheric oxygen on oxanthrol in presence of alkali, the red solution becomes colourless, and anthraquinone is formed. When sodium hydroxide is used, nearly half the total quantity of oxygen taking part in the reaction is converted into sodium peroxide. The peroxide was estimated by means of potassium permanganate. When a $N/4$ solution of barium hydroxide is employed, exactly half the oxygen is found as the peroxide, which separates out, and has no further action on the oxanthrol. Oxidation also takes place with the same rapidity in presence of $N/4$ solutions of ammonia, potassium cyanide, or sodium carbonate, but only very slowly in presence of water alone, and still more slowly in presence of dilute hydrochloric acid. Ozone is not formed, and light has no effect on the oxidation. Dihydrophenanthraquinone, under similar conditions, passes through the green quinhydrone to the yellowish-red phenanthraquinone, half the oxygen forming peroxide. Hydrochrysenequinone and hydoretenequinone behave like hydrophenanthraquinone; the formation of quinhydrone retards the reaction. The intermediate products of the oxidation of the hydroxybenzenes could not be isolated, but the naphthols yield compounds often contaminated with tar. Phenylhydroxynaphthol forms phenylhydroxynaphthaquinone. By the action of oxygen on hydrazobenzene, peroxide is formed, but the reaction takes place too slowly to allow of its progress being followed. Hydrazomethyltriazole, although having strongly basic properties, is oxidised by air in presence of alkali in a manner precisely similar to that of phenols, peroxide and azo-compounds being formed.

In this process of oxidation, the oxygen first attacks the compounds, RH_2 forming R and H_2O_2 , the alkali acting as a catalytic agent, and accelerating the action. The formation of salts does not entirely explain the process, for oxanthrol is oxidised much more rapidly when it is shaken with borax or disodium hydrogen phosphate solution than when water alone is used, although ionisation does not take place, for the solution does not become red. The oxidation of hydrazobenzene is very slow in aqueous alcoholic solution, but is considerably accelerated by the addition of alkali. The acid or basic properties of the compound have no influence on the rapidity of oxidation.

The catalytic action of the alkali is of physiological interest in reference to the absorption of oxygen by blood, and the oxidations effected in it.

E. W. W.

Oxidation of the Nature of Dehydrogenation by means of Ferricyanides: Oxidation of Camphor. By ALEXANDRE ÉTARD (*Compt. rend.*, 1900, 130, 569—571).—The results of various observers show that when carbon compounds containing nitrogen, such as hydratropine, phenylene-ethylenediamine, aminoacetone and conicine, are oxidised by means of alkali ferricyanides, they lose hydrogen, but not carbon. Similarly, when camphor is treated with an alkali ferricyanide at the ordinary temperature, it is converted into camphoric acid.

It is incorrect to speak of strong and weak oxidising agents; the results of oxidation depend on the relative constitution of the oxidising agent and the substance oxidised. C. H. B.

Reaction between Aromatic Aldehydes and the Sodium Derivative of Borneol. By ALBIN HALLER (*Compt. rend.*, 1900, 130, 688—691. Compare Abstr., 1891, 1498; 1899, i, 770).—Benzylidene-*d*-camphor is produced when the sodium derivative of either *d*-borneol or *l*-isoborneol is treated with benzaldehyde; *l*-borneol, however, gives rise to the corresponding derivative of *l*-camphor, the following compounds having been prepared in order to corroborate this observation.

o-Methoxybenzylidene-*l*-camphor, $C_8H_{14} \begin{smallmatrix} C:CH \cdot C_6H_4 \cdot OMe \\ | \\ CO \end{smallmatrix}$, produced

by adding *o*-methoxybenzaldehyde to a solution of the sodium derivative in light petroleum, melts at 92—94°, and has $[\alpha]_D -414^{\circ}58'$ in alcoholic solution, whereas its optical antipodes, dissolved in toluene, gives $+431^{\circ}50'$.

p-Methoxybenzylidene-*l*-camphor melts at 125°, and has $[\alpha]_D -528^{\circ}17'$, whilst the dextrorotatory compound has $467^{\circ}07'$.

Piperonylidene-l-camphor crystallises in needles melting at $159^{\circ}5'$ and has $[\alpha]_D -393^{\circ}8'$; the *d*-modification gives $435^{\circ}40'$.

The discrepancy in the arithmetical values of $[\alpha]_D$ for the antipodal forms is due to the employment of solutions of varying concentrations in different solvents. G. T. M.

Resolution of Racemic Benzylidenecamphor. Isomorphism of the Active Components. By JULES MINGUIN (*Compt. rend.*, 1900, 130, 510—513. Compare Abstr., 1897, i, 163, and 1899, i, 771).—When a crystal of dextrorotatory benzylidene camphor is introduced into a supersaturated toluene solution of the racemic compound, optically active crystals separate which appear to contain variable proportions of the two active components; the specific rotation of the dextrorotatory crystals varies from 178° to 310° , and that of the levorotatory crystals from -130° to -262° ; the active compound has $[\alpha]_D \pm 430^{\circ}$. The two components appear to exist in the same crystal in an unracemised condition, for the mixed crystals, like those of the optically active components, belong to the orthorhombic system, whereas the racemic compound crystallises in the monoclinic system. A levorotatory crystal induces crystallisation in a supersaturated alcoholic solution of the dextrorotatory compound probably because

the racemic compound which is formed is insoluble under these conditions; the addition of a racemic crystal produces no effect and in toluene solutions negative results are obtained in both cases.

The optically active crystals obtained in these experiments melt indefinitely at 78—90°; mixtures of the two antipodes behave in a similar manner, whereas the racemic compound melts at 78° and its active components at 96°.

G. T. M.

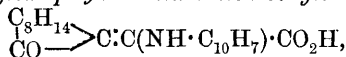
The Vinylamine of the Camphor Group. By PAUL DUDEN and ALFRED E. MACINTYRE (*Ber.*, 1900, 33, 481—483).—When amino-borneol is treated with phosphorus pentachloride, it is converted into

1-chloro-2-camphanamine, $C_8H_{14} \begin{smallmatrix} \text{CH} \cdot \text{NH}_2 \\ \text{CHCl} \end{smallmatrix}$; on covering this base with sodium hydroxide solution, it loses hydrogen chloride, and is converted

into camphenamine, $C_8H_4 \begin{smallmatrix} \text{C} \cdot \text{NH}_2 \\ \text{CH} \end{smallmatrix}$, which readily takes up hydrogen chloride again, and is reconverted into the chloro-base. In favour of the vinylamine constitution for the base, it is urged that (1) it is unsaturated towards alkaline permanganate; (2) the molecular refraction corresponds with one ethylene linking; (3) it interacts with methyl iodide to form a trimethylcamphenamine iodide, $C_{10}H_{15} \cdot NMe_3I$; and (4) it reacts with benzaldehyde (1 mol.) to form a benzylidene compound, $C_{10}H_{15} \cdot N : CHPh$. Benzenesulphocamphenamide, $C_{10}H_{15} \cdot NH \cdot SO_2Ph$, crystallises from a mixture of ether and light petroleum in rhombic tablets and melts at 95—96°; it is practically insoluble in normal sodium hydroxide solution, but an excess of 6—7 per cent. alkali converts it very largely into the sodium salt, which separates in felted needles; the whole of the amide can be extracted from the alkaline mother liquor by adding ether.

T. M. L.

Action of Ethyl Oxalate on Camphor. V. By JOHN BISHOP TINGLE and ALFRED TINGLE (*Amer. Chem. J.*, 1900, 23, 214—230. Compare *Trans.*, 1890, 652; *Abstr.*, 1897, i, 484; 1898, i, 443; 1899, i, 444).—*α-Naphthylcamphoformeneaminecarboxylic acid*,



formed by the action of camphoroxalic acid (1 mol.) on *α*-naphthylamine (0.5 mol.) in alcoholic solution, crystallises from benzene in well-developed, amber prisms containing $\frac{1}{2}$ mol. C_6H_6 ; at 100—105°, the crystals become opaque, then change to a yellow powder which melts and decomposes at 170°. The acid readily dissolves in sodium carbonate solution, but gives no coloration with ferric chloride and alcohol.

β-Naphthylcamphoformeneaminecarboxylic acid, obtained in a manner similar to the *α*-derivative, crystallises from toluene in bright yellow needles melting and decomposing at 173°.

Orthophenylenediamine condenses with camphoroxalic acid, forming a compound, $C_{18}H_{20}O_2N_2$, which crystallises from benzene in bright

yellow needles melting at 246° ; it dissolves slightly in hot water, boiling hydrochloric acid, or sodium hydroxide solution, being practically unacted on by these solvents; concentrated sulphuric acid readily dissolves it in the cold, giving a red coloration.

With semicarbazide hydrochloride, camphoroxalic acid yields two compounds of the composition $\text{C}_8\text{H}_{14}\text{O} \rightarrow \text{C}:\text{C}(\text{NH}\cdot\text{NH}\cdot\text{CO}\cdot\text{NH}_2)\cdot\text{CO}_2\text{H}$. The α -semi-carbazide separates from acetone in small, white needles, melting and decomposing at 218° ; it is soluble in warm sodium carbonate solution, and is reprecipitated in a gelatinous condition on the addition of acid; it gives no coloration with ferric chloride and alcohol, and does not evolve ammonia when heated with caustic alkali solution. The β -isomeride is precipitated from glacial acetic acid solution by the addition of alcohol in the form of cubical aggregates of colourless, microscopic needles, which melt and decompose at $209\text{--}210^{\circ}$; it behaves similarly to the α -compound with ferric chloride and with sodium carbonate, and from solution in the latter, acids precipitate the α -compound.

Ethyl camphoroxalate condenses with aniline hydrochloride in presence of alcoholic potash, yielding *ethyl phenylcamphoformeneaminecarboxylate*, $\text{C}_8\text{H}_{14}\text{O} \rightarrow \text{C}:\text{C}(\text{NHPh})\cdot\text{CO}_2\text{Et}$, which crystallises from benzene in almost white, microscopic needles, melting and decomposing at $158\text{--}160^{\circ}$.

Ethyl β -naphthylcamphoformeneaminecarboxylate, $\text{C}_{21}\text{H}_{22}\text{ON}\cdot\text{CO}_2\text{Et}$, is obtained in a similar manner, using β -naphthylamine in place of aniline; it crystallises from benzene in colourless, microscopic needles which soften at about 160° and melt and decompose at about 174° , the melting point varying with the rapidity of heating.

Ethyl semicarbazylcamphoformeneaminecarboxylate, $\text{C}_{12}\text{H}_{18}\text{O}_2\text{N}_3\cdot\text{CO}_2\text{Et}$, prepared by condensing ethyl camphoroxalate with semicarbazide hydrochloride in presence of potassium acetate and alcohol, dissolves readily in chloroform, ether, or ethyl acetate; from the last-named solvent, it separates in colourless needles melting at 202° .

Phenylcamphoformeneamine reacts with benzoyl chloride in presence of a little sodium hydroxide, yielding a *compound* which crystallises from benzene in cruciform aggregates of prisms melting at $160\text{--}161^{\circ}$. With phenylsulphonic chloride, the amine gives a *substance*, crystallising from benzene in colourless needles, melting at 133° . The action of acetic anhydride on the amine gives rise to a *compound* which separates from a mixture of ethyl acetate and light petroleum in colourless crystals which could not be obtained free from resinous matter; it melts at 134° .

T. H. P.

Genesis of Compounds of the Menthol Series in Plants. By EUGÈNE CHARABOT (*Compt. rend.*, 1900, 130, 518—519. Compare this vol., ii, 101, 241).—Specimens of the essential oil of *Mentha piperita*, obtained from the plant in three stages of growth, were analysed, with the results given on p. 304.

At the commencement, the oil is very rich in free menthol, and

	Oil extracted from the plant before budding.	Oil extracted after the formation of buds.		Oil extracted from the plant in flower.
		(a) Leaves.	(b) Inflorescence	
Sp. gr. at 18°	0.9025	0.9016	0.9081	0.9200
Rotatory power at 18°, <i>l</i> = 100 mm.	- 24° 10'	- 26°	- 20° 15'	- 2° 37'
Menthylesters (calculated to menthyl acetate) ...	3.7 per cent.	10.3 per cent.	7.5 per cent.	10.7 per cent.
Combined menthol	2.9 "	8.1 "	5.9 "	8.4 "
Free "	44.3 "	42.2 "	29.9 "	32.1 "
Total "	47.2 "	50.3 "	35.8 "	40.5 "
Menthone	5.2 "	4.2 "	16.7 "	10.2 "

contains only a small amount of menthone; as the green parts develop, the quantity of combined menthol increases. The results obtained with the third sample of oil indicate that the accumulation of esters takes place only in the leaves, and that, as the oil passes to the flowering parts, the amount of esters diminishes; at the same time, the quantity of menthone increases. The menthol, which is produced during the development of the green parts of the plant, becomes esterified in the leaves, and undergoes oxidation to menthone in the inflorescence. The formation of the latter compound depends on the flowering of the plant; when the reproductive functions are arrested by the action of certain insects, the amount of ketone produced is very small.

G. T. M.

Benzenesulphamino-compounds of Primary Bases. By RICHARD WILLSTÄTTER and RUDOLF LESSING (*Ber.*, 1900, 33, 557—559).—Benzenesulphonic chloride reacts with certain primary bases of the terpene group to form amino-compounds, which, in contradiction to Hinsberg's rule, are insoluble in alkalis. *Benzenesulphondihydrocarvylamide*, $C_{10}H_{17} \cdot NH \cdot SO_2Ph$, crystallises in colourless needles melting at 132°, and is not altered by concentrated aqueous soda. *Benzenesulphondihydroeucarvylamide* crystallises in quadratic tablets melting at 103—105°, and is also insoluble in alkalis.

A. H.

Curangin, the Glucoside of Curanga Amara. By S. E. BOORSMA (*Chem. Centr.*, 1900, i, 298; from *Ned. Tijds. Pharm.*, 11, 366—371. Compare this vol., i, 243).—Curangaegenin, $C_{30}H_{47}O_7$, does not contain methoxy-groups. The formula was confirmed by molecular weight determinations. Curangin is either non-poisonous or only very slightly poisonous.

E. W. W.

Aloe-emodin and Frangula-emodin. By O. A. OESTERLE (*Arch. Pharm.*, 1899, 237, 699—704).—Emodin extracted from *Frangula* bark crystallises in orange-red needles and melts at 250°. It can also be distinguished from aloe-emodin (*Abstr.*, 1899, i, 538) by heating it for a little while with strong sulphuric acid, bringing a few drops of the mixture into water, and making alkaline with ammonia, when a cherry-red solution is formed, which gives an absorption band between 0.56 and 0.47 μ . Under similar circumstances,

aloe-emodin yields a distinctly violet solution, with an absorption band between 0.59 and 0.49μ .

When heated with propionic anhydride, aloe-emodin yields a yellow product melting at 152 — 153° ; the product from frangula-emodin melts at 121 — 122° . When treated with benzoyl chloride and sodium hydroxide, aloe-emodin yields a *tribenzoyl* derivative, whilst frangula-emodin gives a *dibenzoyl* derivative; these are yellow, and melt at 235° and 225° respectively. C. F. B.

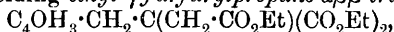
Cause of the Change of Colour of Congo Red by the Action of Acids. By ST. SCHIMANSKY (*Chem. Centr.*, 1900, i, 423; from *Mitt. Technol. Gewerb-Mus. Wien*, 1900, 39—40).—By the action of acids on Congo red, it becomes blue, but this is not due, as hitherto supposed, to the formation of the free dye, but rather to the production of an unstable hydrogen chloride compound, which is gradually decomposed by washing with water. The free dye, which is brownish-red and soluble in water, is prepared by treating a solution with excess of hydrochloric acid, and washing the precipitate with water, until the filtrate acquires a pale pink colour. E. W. W.

A Glycol and Aldol of the Furfuran Series. By GUSTAV LINDAUER (*Monatsh.*, 1900, 21, 72—79).—Furfuraldehyde and isobutaldehyde condense in the presence of alcoholic potash to form γ -furfuryl- $\beta\beta$ -dimethylpropylene glycol, $C_4OH_3 \cdot CH(OH) \cdot CMe_2 \cdot CH_2 \cdot OH$, which is a hygroscopic, colourless substance, melts at 64° , is volatile with steam, and boils at 257° (corr.). The diacetate is a colourless liquid, which boils at 176 — 177° under 42 mm. pressure. The two aldehydes, when shaken together with a cold saturated solution of potassium carbonate, form a thick oil, which cannot be distilled, and is probably the aldol corresponding with the above glycol, which is formed when this oil is reduced by means of aluminium amalgam. R. H. P.

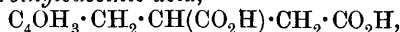
Furfuroylacetic Acid and Methyl Furfuryl Ketone. By S. S. SANDELIN (*Ber.*, 1900, 33, 492—494. Compare Marquis, *Abstr.*, 1899, i, 798).—Ethyl furfuroylacetate, $C_4OH_3 \cdot CO \cdot CH_2 \cdot CO_2Et$, may be obtained by the action of sodium on a mixture of ethyl acetate and ethyl pyromucate, according to Claisen and Lowman's method (*Abstr.*, 1887, 583); it is an almost odourless, greenish-yellow oil distilling at 170° under 33 mm. pressure; its copper derivative, $C_{18}H_{18}O_8Cu$, is a green, microcrystalline powder melting at 175° . When the ester is warmed for several hours on the water-bath with a slight excess of phenylhydrazine, it yields 1-phenyl-3-furfurylpyrazolone, $NPh \begin{matrix} \nearrow N=C \cdot C_4OH_3 \\ \searrow CO \cdot CH_2 \end{matrix}$, crystallising in colourless plates and melting at 179° , and when boiled with sulphuric acid (1 in 25) for some $2\frac{1}{2}$ hours, and then extracted with ether, it yields methyl furfuryl ketone melting at 33° and distilling at 173° , the phenylhydrazone of which melts at 86.5° and the oxime at 92° . When the oxime is treated with Beckmann's mixture, it yields a small quantity of a nitrogen compound melting at 108° , which, when hydrolysed with potassium hydroxide, yields a compound melting at 99° . J. J. S.

Fururysuccinic Acid [**Furfurysuccinic Acid**]. By S. S. SANDELIN (*Ber.*, 1900, 33, 487—489. Compare Abstr., 1898, i, 467).—*Ethyl β-cyano-β-furfurylpropionate*, $C_4OH_3 \cdot CH(CN) \cdot CH_2 \cdot CO_2Et$, is formed when ethyl furfurylmalonate is heated for 7 hours at 60° with an aqueous alcoholic solution of potassium cyanide (1 mol.); it distils at 174·5° under 33 mm. pressure, readily turns brown, and, on hydrolysis with an excess of barium hydroxide, yields furfurylsuccinic acid. *β-Cyano-β-furfurylpropionic acid* is obtained, together with considerable amounts of bye-products, when 2 mols. of potassium cyanide are employed; it crystallises from benzene in needles melting at 109°, dissolves in water, but is insoluble in light petroleum, and is readily hydrolysed to the succinic acid; its *calcium* and *barium* salts are readily soluble in water, whereas the *silver* salt is insoluble, but readily decomposes. When dissolved in hot water, it is hydrolysed to *furfurylsuccinamic acid*, $C_4OH_3 \cdot CH(CO \cdot NH_2) \cdot CH_2 \cdot CO_2H$, which crystallises in colourless needles melting at 155°. The *diamide*, obtained by the action of concentrated ammonia on the methyl ester, crystallises from boiling water in thin plates melting and decomposing above 220°; the *dihydrazide* forms a white powder melting at 159—161°, dissolves readily in water, and yields a *dibenzylidene* derivative, $C_{22}H_{20}O_3N_4$, melting at 199—200°. J. J. S.

Furfurylsuccinic Acid [**Furfurylcarbinylsuccinic Acid**]. By S. S. SANDELIN (*Ber.*, 1900, 33, 489—491).—*Ethyl furfurylcarbinylmalonate*, obtained from the acid (Abstr., 1888, 678) by the aid of sulphuric acid and alcohol, is a pale yellow oil distilling at 171—173° under 33 mm. pressure; it reacts with sodium ethoxide and ethyl chloroacetate, yielding *ethyl γ-furfurylpropane-αββ-tricarboxylate*,



which is a thick, yellowish oil distilling at 212—213·5° under 25 mm. pressure; when hydrolysed with excess of alcoholic potash, it yields the *acid*, which, after solution in ether and precipitation with light petroleum, forms minute needles melting and decomposing at 155—156°. When the acid is heated at 155—160°, it loses carbon dioxide and yields *furfurylcarbinylsuccinic acid*,



crystallising from acetic acid in plates melting at 139·5—140° and insoluble in benzene, chloroform, or light petroleum; the *ethyl* ester is a pale yellow oil distilling at 213·5—215° under 67 mm. pressure.

J. J. S.

Hydroxylamine Derivatives of Tetrahydropyrene Compounds. By PAVEL IW. PETRENKO-KRITSCHENKO (*J. Russ. Phys. Chem. Soc.*, 1899, 31, 901—905, and *Ber.*, 1900, 33, 744—747. Compare Abstr., 1899, i, 706).—*o*-Diethoxydiphenyltetrahydropyroneoxime crystallises with various organic liquids, giving the following compounds. With glycerol, in which it is only slightly soluble, $C_{91}H_{25}O_4N + C_8H_8O_3$, which melts at about 126°. Ethylene glycol readily dissolves the oxime, and deposits shining crystals of the composition $C_{21}H_{25}O_4N + 2\frac{1}{2}C_2H_6O_2$, which melt, when quickly heated, at about 106°. Benzene yields efflorescent crystals of the formula $C_{21}H_{25}O_4N + 1\frac{1}{2}C_6H_6$, and with carbon tetrachloride the compound $C_{21}H_{25}O_4N + 2CCl_4$ is formed. With quinoline, $C_{21}H_{25}O_4N + 2C_9H_7N$, melting at about 104°, is obtained, and

aniline gives $C_{21}H_{25}O_4N + 2\frac{1}{2}C_6H_7N$. Compounds were also obtained with ethyl malonate, ethyl acetoacetate, ether, amyl alcohol, isovaleric acid, ethylene bromide, and nitrobenzene, but in all these cases crystals deposited at different temperatures did not give concordant numbers on analysis.

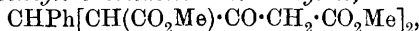
o-Dimethoxydiphenyltetrahydropyroneoxime crystallises with ethyl malonate, ethyl acetoacetate, or acetic acid, forming compounds of indefinite composition.

Diphenyltetrahydropyroneoxime is readily dissolved by ethylene glycol, and the solution deposits shining crystals having the composition $C_{17}H_{17}O_2N + 2C_2H_6O_2$ and melting at 145° . With glycerol, it gives shining needles of the formula $C_{17}H_{17}O_2N + C_3H_8O_3$, and melting at 147° . With ethyl malonate and ethyl acetoacetate, indefinite compounds are obtained.

The *benzoyl* derivative of diphenyltetrahydropyroneoxime, $O \begin{smallmatrix} \text{CHPh} \cdot \text{CH}_2 \\ \text{CHPh} \cdot \text{CH}_2 \end{smallmatrix} \text{C:N} \cdot \text{OBz}$, separates from acetic acid solution in white crystals which melt at 157° and dissolve slightly in alcohol, but are insoluble in water.

T. H. P.

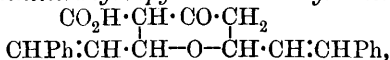
Synthesis of Tetrahydropyrone Derivatives. By PAVEL IW. PETRENKO-KRITSCHENKO and E. ELTCHANINOFF (*J. Russ. Phys. Chem. Soc.*, 1899, 31, 905—909. Compare Abstr., 1899, i, 440).—On condensing benzaldehyde with ethyl acetonedicarboxylate in presence either of hydrochloric acid or ammonia, a mixture of isomeric ethyl diphenyltetrahydropyronecarboxylates is obtained with melting point varying from 116 — 126° ; the solubilities of these isomerides are apparently nearly equal, since they could not be separated by crystallisation. When methyl acetonedicarboxylate is used instead of the ethyl ester in this condensation, in presence of hydrochloric acid, the corresponding methyl derivative, having the composition $C_{21}H_{26}O_6$, and the melting point 194° , is obtained; when ammonia is used as the condensing agent, an isomeric compound melting at 146 — 149° is obtained, which, however, could not be separated from a small quantity of an admixed isomeride. In presence of a few drops of diethylamine, benzaldehyde and methyl acetonedicarboxylate condense to form *methyl benzylidenebisacetonedicarboxylate*,



which melts at 167 — 172° , and is slightly soluble in alcohol, chloroform, or benzene, but insoluble in water; its alcoholic solution gives a faint red colour with ferric chloride.

T. H. P.

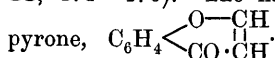
Bis-Phenylethylenetetrahydropyronecarboxylic Acid and its Derivatives. By EDOARDO COEN (*Gazzetta*, 1900, 30, i, 1—8).—2 : 5-Diphenylethylenetetrahydropyrone-3-carboxylic acid,



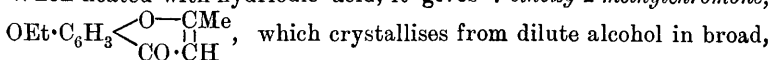
obtained by passing hydrogen chloride into a mixture of 2 mols. of cinnamaldehyde and one of acetonedicarboxylic acid dissolved in acetic acid, separates from benzene as an orange-yellow powder and melts at 210 — 211° ; it is soluble in alcohol, ether, or ethyl acetate. The *bromo-* derivative, $C_{22}H_{19}O_4\text{Br}$, separates from alcohol as a yellow powder melting and decomposing at above 280° , and dissolves in benzene or ether, and, to

a less extent, in alcohol. The *ethyl* ester of the acid, $C_{24}H_{24}O_4$, is precipitated from benzene solution, by the addition of light petroleum, as a yellow powder melting at 233° . By the action of alcoholic ammonia on the ethyl ester, three isomeric *bases*, of the composition $C_{44}H_{41}O_7N$, are obtained. The first of these is a yellow substance, and when crystallised from alcohol melts at $244\text{--}245^\circ$; the second is soluble in ethyl acetate and melts at above 280° ; and the third is insoluble in all solvents. They yield pale yellow, crystalline *platini-chlorides*.
T. H. P.

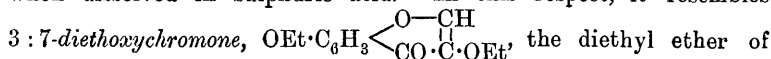
2-Methyl-7-hydroxypheno-3-pyrone (2-Methyl-7-hydroxychromone). By M. BLOCH and STANISLAUS VON KOSTANECKI (*Ber.*, 1900, 33, 471—476).—The name "*chromone*" is introduced for pheno-*y*-



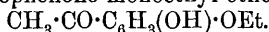
α-Acetyl-2:4-diethoxyacetophenone, $CH_3Ac \cdot CO \cdot C_6H_4(OEt)_2$, is prepared by the action of ethyl acetoacetate on resacetophenone diethyl ether, crystallises from dilute alcohol in colourless prisms, melts at 90° , and gives a red coloration with ferric chloride in alcoholic solution. When heated with hydriodic acid, it gives 7-ethoxy-2-methylchromone,



silky needles, melts at $123\text{--}124^\circ$, and gives a violet-blue fluorescence when dissolved in sulphuric acid. In this respect, it resembles



Schall and Dralle's oxidation product of brazilin (*Abstr.*, 1892, 502; compare Feuerstein and Kostanecki, *Abstr.*, 1899, i, 538), which crystallises in large, flat needles, and melts at 125° . When heated with sodium ethoxide, 7-ethoxy-2-methylchromone is hydrolysed into acetic acid and resacetophenone monoethyl ether,



7-Hydroxy-2-methylchromone, $OH \cdot C_6H_3 \begin{array}{c} \text{O} - \text{CMe} \\ \diagup \quad \diagdown \\ \text{CO} \cdot \text{CH} \end{array}$, is produced in the action of hydriodic acid on acetyldiethoxyacetophenone, along with the ethyl ether already described, from which it can be prepared by the further action of hydriodic acid; it crystallises from dilute alcohol in short, thick, well-formed, microscopic prisms, melts at $249\text{--}250^\circ$, and gives a blue-violet fluorescence when dissolved in sulphuric acid.

T. M. L.

Condensation of Homologous Phloroglucinols with Salicylaldehyde. By HUGO WEIDEL and FRANZ WENZEL (*Monatsh.*, 1900, 21, 62—71).—When dimethylphloroglucinol and salicylaldehyde, dissolved in acetic acid, are heated together with hydrochloric acid, crystals containing hydrochloric acid separate out, which, on treatment with water, decompose and leave 5:7-dimethyl-8-hydroxyfluorone; this crystallises in dark red prisms melting at 275° and yields an *acetyl* derivative, which forms clusters of lustrous, yellow needles, and melts at $208\text{--}210^\circ$; on treatment with potash and methyl iodide, it forms a *pseudomethyl ether*, which crystallises in dull, orange-yellow needles melting at 133° .

Methylphloroglucinol and salicylaldehyde form a similar condensation product, (5-or 7-)methyl-8-hydroxyfluorone, which is a very insoluble substance crystallising only from methyl alcohol in ochreous, microscopic needles melting and decomposing at 220°.

R. H. P.

Ricinine. By THOMAS EVANS (*J. Amer. Chem. Soc.*, 1900, 22, 39—46. Compare Tuson, *Trans.*, 1864, 17, 195, *Werner Jahresber.*, 1870, 877, and Schulze, *Abstr.*, 1898, i, 42).—It appears that the compounds obtained by Tuson and by Schulze are identical; Tuson's method of extraction yields somewhat less satisfactory results than Schulze's, although the product obtained is lighter in colour. It has been found advantageous to substitute boiling toluene for alcohol in Tuson's method. When recrystallised from alcohol, ricinine forms small plates melting at 193°. The analytical data agree fairly well with those obtained by Schulze and point to the composition $C_{16}H_{16}O_4N_4$.

A *dibromide*, probably $C_{16}H_{16}O_4N_4Br_2$, or $C_{16}H_{14}O_4N_4Br_2$, is obtained when ricinine is treated with bromine in either aqueous or chloroform solution; it crystallises in long, brittle needles melting and decomposing at 230°, and is only sparingly soluble in most solvents. Alkaline potassium permanganate readily oxidises ricinine, yielding an acid which crystallises in colourless needles melting at 279—280°, but turns black a few degrees lower. A second oxidation product crystallising in red prisms and soluble in benzene to a reddish-yellow solution with a green fluorescence has also been obtained. J. J. S.

Chloro-derivatives of Oxygenated Alkaloids. Action of Chlorine on Strychnine in Glacial Acetic Acid Solution. By GAETANO MINUNNI and GIOVANNI ORTOLEVA (*Gazzetta*, 1900, 30, i, 39—54).—The principal product obtained by passing chlorine into an acetic acid solution of strychnine is a *tetrachlorostrychnine*, $C_{21}H_{18}O_2N_2Cl_4 + H_2O$, which separates from alcohol in white, prismatic crystals soluble in glacial acetic acid, and very slightly so in alcohol; its *hydrochloride* dissolves in acetic acid. It forms an *oxime*, $C_{21}H_{18}ON_2Cl_4 \cdot N \cdot OH + 2H_2O$, which at 160° loses $\frac{1}{2}H_2O$ and begins to decompose; it is soluble in alkali hydroxide solution, and is reprecipitated by acids. The *hydrochloride* of the oxime, $C_{21}H_{19}O_2N_3Cl_4 \cdot HCl + 2\frac{1}{2}H_2O$, is slightly soluble in boiling alcohol, from which it may be crystallised.

Besides the tetrachloro-derivative, a small quantity of a *hexachlorostrychnine*, $C_{21}H_{16}O_2N_2Cl_6$, is also obtained; it is a white compound readily soluble in glacial acetic acid. T. H. P.

Pyrrolealdehyde. By EUGEN BAMBERGER and G. DJIERDJIAN (*Ber.*, 1900, 33, 536—542).—Reimer's reaction takes place with pyrrole, giving rise to *pyrrole-2-aldehyde*, $\begin{array}{c} \text{CH} \cdot \text{NH} \\ | \\ \text{CH} \cdot \text{CH} \end{array} > \text{C} \cdot \text{CHO}$; this melts at 45°, and, unlike benzaldehyde, forms large, colourless, rhombic crystals, is odourless, does not redden magenta which has been decolorised by sulphurous acid, and is not oxidised by the air; with alkaline potassium permanganate, it yields pyrroline-2-carboxylic acid (Ciamician and Silber, *Abstr.*, 1884, 1044), a fact which determines its structure. The sodium hydrogen sulphite derivative, $C_5H_6O_4NSNa$, crystallises

from water in lustrous leaflets, and the *phenylhydrazone* from light petroleum in white, shining needles melting at 139—139.5°; the *p*-nitrophenylhydrazone crystallises from xylene in reddish-black needles with an intense, steel-blue surface-colour, and melts at 182.5—183°. The author emphasises the fact that the latter compound gives brownish-yellow solutions with chloroform, xylene, carbon tetrachloride, or ether, although with methyl or ethyl alcohol, glacial acetic acid, or ethyl acetate dark red solutions are obtained; the explanation is, perhaps, to be sought for in the different dissociating powers of the solvents named. The *p*-nitrophenylhydrazones of a large number of other ketones and aldehydes show a similar behaviour; that derived from diacetyl, $C_{10}H_{11}O_3N_3$, hitherto undescribed, forms orange-yellow needles with a silky lustre, and melts at 229.5—230.5°. *Pyrrole-aldoxime* crystallises from chloroform or benzene in white, silky needles and melts at 164.5°. W. A. D.

Derivatives of 5:6:8-Trimethylquinoline. By HJALMAR WIKANDER (*Ber.*, 1900, 33, 646—648).—5:6:8-Trimethylquinoline methiodide, $C_{12}H_{13}N, MeI$, crystallises from water in large, yellow, prismatic rods and needles melting and decomposing at 208—209°. The methodichromate, $(C_{12}H_{13}NMe)_2Cr_2O_7$, separates from aqueous solution in small, yellow, sparkling needles which darken at 206° and explode at 216°. The methochloride, $C_{12}H_{13}N, MeCl + 1\frac{1}{2}H_2O$, dissolves in alcohol, and on precipitating with ether separates in small, bluish-green, prickly prisms which soften at 82° and melt at 135°. The base yields a dibromide, $C_{12}H_{13}NBr_2$, which crystallises from acetic acid in large, dark yellow, needles.

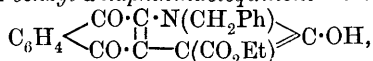
5:6:8-Trimethyltetrahydroquinoline, $C_{12}H_{17}N$, obtained by reducing the trimethylquinoline, is a thick, strongly-smelling oil, boiling at 287—290°. Its hydrochloride crystallises from water in a felt-like mass of small needles which soften at 230° and melt and decompose at 238—239°. T. H. P.

Syntheses of 2- and 4-Hydroxyquinolines. By RUDOLF CAMPS (*Arch. Pharm.*, 1899, 237, 659—691).—Most of the results detailed in this paper have been already published (this vol., i, 115), but the following compounds appear to have been described for the first time. *Propionyl-o-flavaniline* is yellowish, and melts at 137°; *butyryl-o-flavaniline* is white, and melts at 104°. 2-Hydroxy-4-methyl-3-ethylquinoline melts at 226°; 4-hydroxy-2-propylquinoline melts at 166°, and the orange *platinichloride* melts and decomposes at 228°. 2-Hydroxy-4-phenylquinoline melts at 259°, and has only feeble acid and basic properties; when distilled with zinc-dust in a current of hydrogen gas, it yields 4-phenylquinoline. C. F. B.

Malonic Acid Derivatives of Dibromo- α -naphthaquinone. By CARL T. LIEBERMANN [and in part E. HOYER] (*Ber.*, 1900, 33, 566—578. Compare *Abstr.*, 1899, i, 522).—*Ethylamine* 1-ethyl-naphthindolinonequinone-3-carboxylate forms lustrous, steel-blue prisms; the sodium salt crystallises in the form of dark blue needles, and the copper salt is precipitated as red clots from a solution of copper acetate. α -Bromonaphthaquinone-3-ethylacetamide, obtained as a bye-product in

the formation of ethyl ethylnaphthindolinonequinonecarboxylate, (*loc. cit.*) forms red prisms. This ester, on hydrolysis, yields 2-hydroxy-1-ethylnaphthindolequinone, $C_6H_4 \begin{smallmatrix} \text{CO} \cdot \text{C} \cdot \text{N} \text{Et} \\ | \\ \text{CO} \cdot \text{C} - \text{CH} \end{smallmatrix} \rangle \text{C} \cdot \text{OH}$, which from its solution in caustic alkalis is precipitated by acids as a blue powder closely resembling indigotin as regards its solubilities and behaviour with sulphuric acid; it does not, however, colour mordants.

Ethyl 2-hydroxy-1-benzyl-a-naphthindolequinone-3-carboxylate,



prepared by the action of benzylamine on ethyl 2-bromo-*a*-naphthaquinone-3-malonate, forms yellow, silky needles, which melt about 160° , colours mordants, and, on hydrolysis, yields 2-hydroxy-1-benzyl-*a*-naphthindolequinone.

Ethyl bromo-*a*-naphthaquinoneacetoacetate condenses with ethylamine to form the *ethylamide* of 2-methyl-1-ethylnaphthindolequinone-3-carboxylic acid, $C_6H_4 \begin{smallmatrix} \text{CO} \cdot \text{C} - \text{N} \text{Et} \\ | \\ \text{CO} \cdot \text{C} \cdot (\text{CO} \cdot \text{NH} \text{Et}) \end{smallmatrix} \rangle \text{C} \text{Me}$, which forms lustrous, dark steel-blue needles.

2-Hydroxy-*a*-naphthaquinone-3-acetic acid, $C_6H_4 \begin{smallmatrix} \text{CO} \cdot \text{C} \cdot \text{OH} \\ | \\ \text{CO} \cdot \text{C} \cdot \text{CH}_2 \cdot \text{CO}_2\text{H} \end{smallmatrix}$, prepared by treating ethyl bromo- or chloro-*a*-naphthaquinonemalonate with alkalis, forms bright yellow tablets, which melt at $206-207^\circ$; the sodium, copper, and ethylamine salts were prepared and analysed; the monomethyl ester forms bright yellow needles melting at $144-145^\circ$.

By the action of alcoholic potash on ethyl bromonaphthaquinoneacetoacetate, a compound, $C_{13}H_9O_3Br$, is obtained as a yellow, crystalline substance melting at 134° ; its solutions in alkali hydroxides or carbonates show strong fluorescence. Its monoethyl ester melts at 180° , the monomethyl ester at 158° , but neither exhibit the fluorescence of the parent substance.

Ethyl a-naphthaquinonedimalonate, $C_6H_4 \begin{smallmatrix} \text{CO} \cdot \text{C} \cdot \text{CH}(\text{CO}_2\text{Et})_2 \\ | \\ \text{CO} \cdot \text{C} \cdot \text{CH}(\text{CO}_2\text{Et})_2 \end{smallmatrix}$, forms yellow crystals which melt at 98° and dissolve in alkalis with green fluorescence; alkalis convert it into *ethyl a-naphthaquinoneisoindonedicarboxylate*, $C_6H_4 \begin{smallmatrix} \text{CO} \cdot \text{C} \cdot \text{CH}(\text{CO}_2\text{Et}) \\ | \\ \text{CO} \cdot \text{C} \cdot \text{CH}(\text{CO}_2\text{Et}) \end{smallmatrix} \rangle \text{CO}$, which crystallises in dark green needles with a violet iridescence.

Ethyl 2-acetonyl-a-naphthaquinone-3-acetate, $C_6H_4 \begin{smallmatrix} \text{CO} \cdot \text{C} \cdot \text{CH}_2 \cdot \text{COMe} \\ | \\ \text{CO} \cdot \text{C} \cdot \text{CH}_2 \cdot \text{CO}_2\text{Et} \end{smallmatrix}$, prepared by leaving a mixture of dibromonaphthaquinone (1 mol.), ethyl acetoacetate (1 mol.), and sodium ethoxide (2 mols.) overnight, crystallises in red needles melting at 158° .
R. H. P.

Action of Iodine on Antipyrine. By J. BOUGAULT (*J. Pharm.*, 1900, [vi], 11, 97—100).—The author's method for the estimation of antipyrine (Abstr., 1899, ii, 193) is also applicable to the estimation

of hypnal and salipyrine, 1 gram of the former absorbing 0.7185 gram of iodine, and 1 gram of the latter 0.7791 gram of iodine.

When concentrated alcoholic solutions of 4 mols. of antipyrine, 4 mols. of iodine, and 3 mols. of mercuric chloride are heated to 70—80° and then mixed together, the compound $4C_{11}H_{11}ON_2I, HgCl_2, HgI_2, 2HCl$ is gradually deposited as a light yellow, crystalline powder. If, however, only 2 mols. of mercuric chloride are used for every 4 mols. of antipyrine, then the bright yellow, crystalline compound, $2C_{11}H_{11}ON_2I, HgI_2, HCl$, is obtained. H. R. LE S.

Iodoantipyrine. By J. BOUGAULT (*J. Pharm.*, 1900, [vi], 11, 100—102. Compare Abstr., 1886, 158).—Pure iodoantipyrine may be obtained by decomposing the compound $4C_{11}H_{11}ON_2I, HgCl_2, HgI_2, 2HCl$ with a solution of potassium iodide made alkaline with a little sodium carbonate. It may also be readily prepared by adding iodine, dissolved in a solution of potassium iodide, to a boiling solution of antipyrine and sodium acetate in water. On cooling the mixture, the iodoantipyrine is precipitated in almost theoretical amount.

100 c.c. of water at 17° dissolve 0.080 gram of antipyrine.

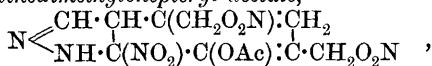
H. R. LE S.

1-Phenyl-4-methylpyrazolone. By FRITZ FICHTER, JOSEPH ENZENAUER, and EMIL UELLENBERG (*Ber.*, 1900, 33, 494—499).—When an aqueous solution of citradibromopyrotartaric acid (1 mol.) is warmed on the water-bath with phenylhydrazine (3 mols.), carbon dioxide is evolved, and a deposit of Knorr's 1-phenyl-3-methylpyrazolone-4-azobenzene (Abstr., 1887, 602) and 1-phenyl-4-methyl-5-pyrazolone is formed; the two may be separated by the aid of benzene, in which the azo-derivative is soluble. The same phenylmethylpyrazolone is obtained when Wislicenus and Arnold's 1-phenyl-4-methylpyrazolone-3-carboxylic acid (*Annalen*, 1888, 246, 331) is distilled under 9 mm. pressure, or when ethyl-β-bromo-α-methylacrylate is heated at 120—130° with phenylhydrazine. The latter synthesis indicates that bromomethylacrylic acid is probably an intermediate product in the preparation of the pyrazolone from citradibromopyrotartaric acid. 1-Phenyl-4-methyl-5-pyrazolone, $NPh \begin{matrix} \text{NH} \cdot \text{CH} \\ \diagup \quad \diagdown \\ \text{CO} \cdot \text{CMe} \end{matrix}$, crys-

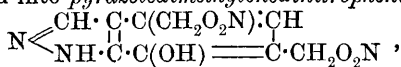
tallises from alcohol in glistening, flat needles melting at 210°, and dissolves readily in both alkalis and acids, but does not react with nitrous acid, or yet with diazobenzene (Abstr., 1895, i, 395); with bromine, it yields a 4-bromo-1-phenyl-4-methyl-5-pyrazolone melting at 242°, and with benzaldehyde a benzylidene derivative melting and decomposing at 216—225°.

In the synthesis of 1-phenyl-4-methyl-5-pyrazolone from ethyl bromomethylacrylate, an isomeric base, 1-phenyl-4-methyl-3-pyrazolone, is always formed; in fact, it is the main product when the condensation takes place on the water-bath; it crystallises in glistening needles melting at 145°, yields a nitro-derivative which crystallises in yellow, glistening needles melting at 124°, an acetyl derivative, 2-acetyl-1-phenyl-4-methyl-3-pyrazolone, melting at 167°, and also reacts with diazobenzene J. J. S.

Action of Diazomethane on Picryl Acetate. By HANS VON PECHMANN (*Ber.*, 1900, 33, 627—631. Compare Heinke, *Abstr.*, 1898, i, 413).—*Pyrazolinedimethylenepicryl acetate*,



and *trimethylenepicryl acetate*, $\text{CH}_2 \begin{array}{c} \text{CH} \cdot \text{C}(\text{CH}_2\text{O}_2\text{N}) \cdot \text{CH} \\ \diagdown \text{C}(\text{NO}_2) \cdot \text{C}(\text{OAc}) \cdot \text{C} \cdot \text{CH}_2\text{O}_2\text{N} \end{array}$, are both obtained when powdered picryl acetate is added to an ethereal solution of diazomethane, and may be separated by careful treatment with cold acetone and water, in which the pyrazole derivative is the less soluble. Pyrazolinedimethylenepicryl acetate forms pale yellow, six-sided prisms melting and decomposing at 144° , is only sparingly soluble in alcohol, ether, or benzene, and when warmed with concentrated hydrochloric acid, or, still better, with alcohol and hydrochloric acid, is converted into *pyrazoledimethylenedinitrophenol*,



which crystallises from acetic acid in colourless prisms melting at 239.5° , and when oxidised with nitric acid yields pyrazole-4:5-dicarboxylic acid (*Abstr.*, 1899, i, 948). Trimethylenepicryl acetate crystallises from dilute acetone or alcohol in colourless needles melting at $140\text{--}141^\circ$; it dissolves readily in the usual solvents, and when warmed with dilute sulphuric acid, yields hydroxylamine. The constitution of the group $\text{CH}_2\text{O}_2\text{N}$ is not known. J. J. S.

Diaminodixenylamine. By VICTOR MERZ and H. STRASSER (*J. pr. Chem.*, 1900, [ii], 61, 103—107).—*Diaminodixenylamine* [*di-p-amino-di-diphenylamine*], $\text{NH}(\text{C}_6\text{H}_4 \cdot \text{C}_6\text{H}_4 \cdot \text{NH}_2)_2$, prepared by heating a mixture of benzidine and finely-divided benzidine hydrochloride in a current of carbon dioxide at $330\text{--}340^\circ$, distils at $370\text{--}380^\circ$ under 2.5 mm. pressure, dissolves readily in hot aniline, and crystallises from a large volume of benzene in minute, white flakes; it blackens when heated in the air, but when heated in a sealed tube melts at $220\text{--}221^\circ$; it forms a *hydrochloride*, $\text{C}_{24}\text{H}_{21}\text{N}_3 \cdot 2\text{HCl}$.

T. M. L.

Glauconic Acids. II. By OSCAR G. DOEBNER (*Ber.*, 1900, 33, 677—680. Compare *Abstr.*, 1898, i, 384).—Glauconic acids have been prepared from *p*-toluidine and *p*-anisidine; the methods were those employed previously, except that it was found best to oxidise the hydroglauconic to the glauconic acid by means of a concentrated solution of potassium ferricyanide, avoiding an excess.

From *p*-toluidine: *Hydro-6-methylglauconic acid* melts at 272° ; *dihydro-6-methylquinaldine*, also obtained by distilling 6-methylquinaldine with zinc dust, smells like aniseed, boils at $262\text{--}264^\circ$, and forms a *picrate* melting at 153° ; 6-methylglauconic acid forms dark blue flocks and yields alkali salts, crystallising in slender, blue needles.

From *p*-anisidine: 6-Methoxyhydroglauconic acid is brownish-yellow, and melts and decomposes at $228\text{--}230^\circ$; 6-methoxyglauconic acid forms dark blue flocks; its alkali salts crystallise in blue needles with a

coppery lustre and dissolve in water and alcohol with a bluish-red fluorescence. C. F. B.

Action of Tetramethyldiaminobenzophenone on α -Dinaphthylbenzidine. By VICTOR MERZ and H. STRASSER (*J. pr. Chem.*, 1900, [ii], 61, 107—109).— α -Naphthylbenzidine condenses with 1 mol. only of tetramethyldiaminobenzophenone when the mixture reacts in naphthalene solution with phosphorus oxychloride; the product is a dark copper-coloured pigment with a metallic lustre, and is regarded as having the constitution

$$\text{C}_{10}\text{H}_7\cdot\text{NH}\cdot\text{C}_6\text{H}_4\cdot\text{C}_6\text{H}_4\cdot\text{NHCl}:\text{C}_{10}\text{H}_6\cdot\text{C}(\text{C}_6\text{H}_4\cdot\text{NMe}_2)_2;$$
 it was not isolated in a pure state. T. M. L.

Dihydro-1:2:3:4-tetrazine (Osotetrazine). By HANS VON PECHMANN and WILHELM BAUER (*Ber.*, 1900, 33, 644—646).—*Dibenzoyldimethyl-osotetrazine*, $\begin{matrix} \text{CMe}\cdot\text{N}\cdot\text{NBz} \\ | \\ \text{CMe}\cdot\text{N}\cdot\text{NBz} \end{matrix}$, obtained by oxidising diacetyldi-

benzoylosazone, crystallises in white needles melting at 140° . On removing the benzoyl groups by means of hydrochloric acid, first *benzoyldimethyl-osotetrazine*, forming white, nodular crystals melting at 95° , is obtained, and finally *dimethyl-osotetrazine*, $\text{C}_4\text{H}_8\text{N}_4$, which crystallises, on adding light petroleum to its benzene solution, in colourless leaflets which melt at 95° and explode when quickly heated. Dimethyl-osotetrazine is soluble in most solvents, its aqueous solution having a neutral reaction. With mercuric chloride, it gives a white *precipitate*, which crystallises from hot water in needles melting at 146 — 147° . Ferric chloride colours the solution yellowish-red, whilst on adding silver nitrate, colourless needles are slowly deposited. On boiling, it reduces Fehling's solution and alkaline silver solutions, and, when acted on by sulphuric acid and dichromate, undergoes vigorous oxidation, even in the cold. T. H. P.

Conversion of Tetrazine into Triazole Derivatives. By MAX BUSCH and CARL HEINRICHS (*Ber.*, 1900, 33, 455—463. Compare Hantzsch and Silberrad, this vol., i, 261).—*Diethyl diphenylcarbazide-dicarboxylate*, $\text{CO}(\text{NPh}\cdot\text{NH}\cdot\text{CO}_2\text{Et})_2$, prepared by the action of carbonyl chloride on ethyl phenylcarbazine, crystallises from light petroleum in white needles and melts at 194° .

Phenylurazine, $\text{CO}\begin{matrix} \text{NPh}\cdot\text{NH} \\ \diagup \quad \diagdown \\ \text{NH} \quad \text{N} \end{matrix}\text{C}\cdot\text{OH}$, prepared by the action of carbethoxyphenylhydrazinecarboxylic chloride, $\text{COCl}\cdot\text{NPh}\cdot\text{NH}\cdot\text{CO}_2\text{Et}$, on hydrazine hydrate, crystallises from water in large needles, and from alcohol in glistening flakes, melts at 244 — 245° , dissolves readily in alkali hydroxides or carbonates, has no basic properties, is not attacked by ferric chloride or mercuric oxide, and gives no definite oxidation product with potassium permanganate or with nitric acid; the *potassium* and *sodium* salts crystallise in glistening needles; the *triacetyl* derivative crystallises from alcohol in beautiful, colourless flakes and melts at 128° . With benzaldehyde, phenylurazine forms an

additive compound, $\begin{matrix} \text{NH}\cdot\text{CO}\cdot\text{N} \\ | \quad \diagup \quad \diagdown \\ \text{NPh}\cdot\text{CO}\cdot\text{N} \end{matrix}\text{CHPh}$, or $\text{N}\begin{matrix} \diagup \quad \text{CO}\cdot\text{NPh} \\ \diagdown \quad \text{CHPh} \\ \diagup \quad \text{N}\cdot\text{C}(\text{OH}) \end{matrix}$, which

crystallises from alcohol in glistening flakes, melts at 175° , dissolves in dilute sodium hydroxide, and is decomposed by dilute acids. The *methyl ether* crystallises from alcohol, benzene, or water, melts at $135-136^{\circ}$, is readily decomposed by alkalis, and has no basic properties. By the action of nitrous acid, phenylurazine is converted

into phenylurazole, $\text{NPh} \begin{array}{c} \text{N}=\text{C}\cdot\text{OH} \\ \diagup \\ \text{CO}\cdot\text{NH} \end{array}$ (Pinner, Abstr., 1887, 1043);

the methyl ether similarly gives a *methyl phenylurazole*, to which the formula $\text{NPh} \begin{array}{c} \text{N}=\text{C}\cdot\text{OMe} \\ \diagup \\ \text{CO}\cdot\text{NH} \end{array}$ or $\text{NPh} \begin{array}{c} \text{N}=\text{C}\cdot\text{OMe} \\ \diagup \\ \text{C}(\text{OH})\cdot\text{N} \end{array}$ is assigned;

this crystallises from water in snow-white, glistening flakes, melts at $182-185^{\circ}$, and, unlike methylurazine, has acid properties, and dissolves in alkali carbonates. T. M. L.

Diazotisation of Safranine. By GEORGE F. JAUBERT (*Compt. rend.*, 1900, **130**, 661—663).—The red, or monoacid, and the blue, or diacid, salts of phenosafranin are shown by titration with sodium nitrite solution to yield only monodiazotised-derivatives; they therefore contain a single amino-group capable of diazotisation and possess a paraquinonoid structure. On the other hand, the green, or triacid, salts, which are stable only in concentrated acid solution, react with twice the quantity of sodium nitrite to form a bisdiazotised-derivative, and have therefore the orthoquinonoid structure of an azonium base. N. L.

Oxidation of Hydrazobenzene in Alkaline Alcoholic Solution by Atmospheric Oxygen. By AUGUSTIN BISTRZYCKI (*Ber.*, 1900, **33**, 476. Compare Bamberger, this vol., i, 220).—The oxidation of hydrazobenzene by atmospheric oxygen is greatly facilitated by adding alkali to the alcoholic solution. T. M. L.

Transformation of Bromodiazonium Chlorides into Chlorodiazonium Bromides. By ARTHUR HANTZSCH and J. S. SMYTHE (*Ber.*, 1900, **33**, 505—522).—It is shown that certain *o*-bromodiazonium chlorides are readily transformed, either in the dry state or in solution, into *o*-chlorodiazonium bromides, by an intramolecular change. A similar, but slower, interchange also occurs when the halogen atoms are in the para-position relatively to one another, but no such change takes place between groups in the meta-position; thus 2:6-dibromobenzenediazonium chloride is more rapidly transformed than the 2:4-dibromo-compound, and 3:5-dibromotoluene-4-diazonium chloride than 3:5-dibromotoluene-2-diazonium chloride. Moreover, in the case of 2:4-dibromodiazonium chloride ($\text{N}_2\text{Cl}=1$) there is formed a greater proportion of 1-chloro-4-bromo- than of 4-chloro-1-bromo-diazonium bromide. Experiments with 2:4:6-tribromodiazonium chloride show that the rate of transformation in solution is apparently inversely proportional to the dissociating power of the solvent; thus it is most rapid in ethyl alcohol, less so in glacial acetic acid, still less in methyl alcohol, and is almost zero in aqueous solution. Experiments with the same salt in methyl alcoholic solution show that the transformation occurs according to the equation $k = 1/t \cdot \log. a/a-x$ characteristic of a unimolecular reaction; this, taken in conjunction with the inhibiting

action of dissociating solvents, proves that the change is *intra*- and not *inter*-molecular.

By increasing the number of bromine atoms in the benzene nucleus, the rate of interchange of chlorine and bromine is greatly accelerated; thus both *o*- and *p*-bromodiazonium chlorides remain unchanged in alcoholic solution, although 2:4- and 2:6-dibromobenzenediazonium chlorides and 3:5-dibromotoluene-2- and -4-diazonium chlorides are rapidly transformed. With 2:4:6-tribromobenzene- and 2:4:6-tribromotoluene-3-diazonium chlorides, the action is still more rapid, whilst all attempts to prepare pentabromobenzenediazonium chloride free from the isomeric bromide formed by transformation were fruitless. On diazotising pentabromoaniline hydrochloride in ethereal solution and subsequently boiling with alcohol, 2:4:6-trichlorodibromobenzene (m. p. 119°) is formed.

A methyl group in the ortho- or para-, or even in the meta-position relatively to the diazo-group diminishes the tendency towards interchange between chlorine and bromine; increasing the dilution has the same effect, whilst raising the temperature greatly accelerates the transformation. In aqueous solution, the rate of transformation is increased by increasing the number of free halogen ions, or more markedly by increasing the number of hydrogen ions.

The diazo-salts of pentabromoaniline can be isolated only with difficulty; the *diazo-nitrate* is described, but attempts to prepare the diazo-bromide yielded only the *perbromide*, $C_6Br_5 \cdot N_2 \cdot Br_3$, as a crystalline powder exploding at 170°; this perbromide, when boiled with alcohol, yields hexabromobenzene, and treatment with aqueous ammonia gives rise to *pentabromodiazobenzeneimide*, $C_6Br_5 \cdot N_3$, which decomposes at about 155°.

W. A. D.

Cause of Ehrlich's Diazo-reaction [in Urine]. By LUDWIG BRIEGER (*Chem. Centr.*, 1900, i, 373; from *Med. Woch.*, 1900, 6).—The author has attempted to isolate the substance which causes the diazo-reaction. Urine from patients suffering from phthisis and typhoid was precipitated with lead acetate, and the precipitate decomposed by means of hydrogen sulphide. The filtrate was then evaporated in a vacuum to a syrup which gave a strong diazo-reaction. The phosphates were removed by means of ammonia and alcohol, and the filtrate evaporated; the residue was dissolved in water and the filtrate yielded with alcohol a deliquescent precipitate which showed the diazo-reaction in a high degree. It is non-poisonous. The author has not as yet succeeded in obtaining a perfectly pure product (compare Clemens, this vol., i, 227).

L. DE K.

A Cuprous Salt of Diazoaminobenzene. By LOUIS MEUNIER and A. RIGOT (*Bull. Soc. Chim.*, 1900, [iii], 23, 103—106).—When a concentrated alcoholic solution of diazoaminobenzene is agitated for about 12 hours with freshly prepared powdered copper, and the product washed with alcohol and finally exhausted with boiling benzene, a *compound*, $Cu_2(NPh \cdot N : NPh)$, is obtained which crystallises in orange-yellow needles, decomposes at 270°, and is insoluble in water, alcohol, ether, or light petroleum. When treated with hydrogen sulphide in benzene solution, it is decomposed, with production of

cuprous sulphide and diazoaminobenzene; it is also decomposed by dilute acetic and hydrochloric acids, with the liberation of two-thirds of the nitrogen, and by nitric acid with explosion and incandescence. If, however, dry hydrogen chloride is passed into the benzene solution of the compound, an unstable, yellowish-white substance, of the composition $\text{Cu}_2(\text{NPhHCl} \cdot \text{N} \cdot \text{NPh})$, is precipitated; this is soluble in water.

Sodium diazoaminobenzenedi-*p*-disulphonate reacts with powdered copper to form an amorphous, orange-yellow compound which is soluble in water, and is decomposed by hydrogen sulphide and by dilute acetic acid. A similar substance, for which no solvent could be found, appears to be formed from *p*-dinitrodiazoaminobenzene.

N. L.

The Condition of Nitrogen in the Proteid Molecule. By WALTHER HAUSMANN (*Zeit. physiol. Chem.*, 1900, 29, 136—145. Compare Abstr., 1899, i, 653).—A number of other proteids have now been subjected to analyses on the plan previously adopted. The following table gives the main results:—

Proteid.	Amidic nitrogen, per cent.	Diamino- nitrogen, per cent.	Monamino- nitrogen, per cent.
Casein	13·37	11·71	75·98
Crystallised egg albumin	8·53	21·33	67·80
Oxyhæmoglobin (horse).....	6·18	23·51	63·26
Serum-globulin (horse).....	8·9	24·95	68·28
Proto-albumose (from fibrin) ..	7·14	25·42	68·17
Globin (horse)	4·62	29·37	67·08
Proteids of pine seeds	10·3	32·8	56·90
Gelatin	1·61	35·83	62·56
Edestin	10·25	38·15	54·99
Hetero-albumose (from fibrin)	6·45	38·93	57·40

W. D. H.

Proportion of Basic Nitrogen in Elastin. By ALLAN C. EUSTIS (*Proc. Amer. Physiol. Soc.*, Dec., 1899; *Amer. J. Physiol.*, 1900, 3, xxi).—The proportion of basic nitrogen split off from elastin by hydrochloric acid is differently given by different observers. Five experiments are here recorded, and the results vary from 0·86 to 17·69 per cent.

The conclusion is drawn that the method in use for the separation of hexon bases by phosphotungstic acid is untrustworthy quantitatively.

W. D. H.

Mucin from Bone. By WILLIAM J. GIES (*Proc. Amer. Physiol. Soc.*, Dec., 1899; *Amer. J. Physiol.*, 1900, 3, vii—viii).—After the removal of the inorganic substances from bone, lime-water extracts from the residue a mucin-like substance. Young formerly failed to obtain mucin; he did not, however, first remove the inorganic substances (Abstr., 1893, ii, 134).

W. D. H.

Mucin. By P. A. LEVENE (*Proc. Amer. Physiol. Soc.*, Dec., 1899; *Amer. J. Physiol.*, 1900, 3, viii).—The acid properties of mucins are not

explained on the general supposition that a mucin is a compound of proteid and carbohydrate. Both tendon mucin and submaxillary mucin yield an acid substance on decomposition. It contains sulphur, and preliminary experiments indicate it to be a substance similar to chondroitin-sulphuric acid, in which the sulphuric acid is in ethereal combination.

W. D. H.

Basic Decomposition Products of Edestin. By P. A. LEVENE and LAFAYETTE B. MENDEL (*Proc. Amer. Physiol. Soc.*, Dec., 1899; *Amer. J. Physiol.*, 1900, 3, iv).—Pure crystallised edestin was decomposed by hydrochloric acid and stannous chloride. In the phosphotungstic acid precipitate, the bases histidine, lysine, and arginine were separated by Kossel's method.

W. D. H.

Ovarial Mucoids. By J. B. LEATHES (*Chem. Centr.*, 1900, i, 45; from *Arch. exp. Path. Pharm.*, 43, 245—258).—Paramucosin, $C_{12}H_{23}O_{10}N$, probably $OH \cdot CH_2[CH(OH)]_4 \cdot CH \cdot N \cdot CH(CHO) \cdot [CH(OH)]_3 \cdot CH_2 \cdot OH$, obtained from Mitjukoff's paramucin (*Arch. Gynakol.*, 49, 278) by means of the copper alkali method, possesses reducing properties and when decomposed by hydrochloric acid yields a simple osamine and not a glucosamine. By boiling the impure paramucosin, from which the albumin has been removed, with potassium hydroxide solution, a base is formed which may be easily separated from paramucosin by boiling the copper compound. Like protamine, this base gives the biuret reaction. It is precipitated by phosphotungstic acid, but not by ferrocyanic or nitric acid and does not give Millon's reaction.

E. W. W.

Cyano-methæmoglobin and Photo-methæmoglobin. By JOHN SCOTT HALDANE (*J. Physiol.*, 1900, 25, 230—232).—Bock (*Skand. Arch. Physiol.*, 6, 299) prepared, by the influence of light on methæmoglobin crystals, a red substance giving a spectrum very much like that of hæmoglobin; it is crystallisable and he termed it photo-methæmoglobin. Kobert (*Maly's Jahreshb.*, 1891, 443) found that when hydrocyanic acid or a cyanide is added to a solution of methæmoglobin, a similar red colour is obtained; this may be used as a delicate test for hydrocyanic acid. The present research shows the two substances are identical; the action of light is to liberate hydrocyanic acid from the potassium ferricyanide used to prepare methæmoglobin. Cyano-methæmoglobin is doubtless a cyanogen compound of hæmoglobin, but there is no displacement of oxygen. It is not identical with Hoppe-Seyler's cyanhæmatin as stated by Szigeti (*Maly's Jahreshb.*, 1893, 620).

W. D. H.

Neutral Hæmatin. By V. ARNOLD (*Zeit. physiol. Chem.*, 1900, 29, 78—85).—Neutral hæmatin, which has not been described before, is of a yellowish-red colour; the yellow tint, as in oxyhæmoglobin, being more pronounced on dilution. It shows two absorption bands rather nearer the violet end of the spectrum than those of oxyhæmoglobin. It can be obtained from oxyhæmoglobin or more readily from methæmoglobin solution by adding sodium chloride and then from a third to a half the volume of alcohol; the presence of the salt prevents precipitation by the alcohol. It may also be obtained

by neutralising a solution of alkaline hæmatin, and dissolving out with alcohol in the presence of salt; dilution with water precipitates it. By heat, the red colour is changed to brown, and the spectrum of alkaline hæmatin is seen; the colour and absorption bands of neutral hæmatin return on cooling.

W. D. H.

Decomposition Products of Hæmatin. By WILLIAM KÜSTER (*Zeit. physiol. Chem.*, 1900, 29, 185—192. Compare Abstr., 1899, i, 468, and this vol., i, 68).—It appeared probable in former work that the substance $C_3H_8O_5$ was not a primary oxidation product of hæmatin, but was due to secondary changes occurring in the dibasic hæmatic acid, $C_3H_9NO_4$. This view is now confirmed by further experiments.

W. D. H.

Preparation of α - and β -Nucleic Acid, and of Nucleothymic Acid. By ALBERT NEUMANN (*Chem. Centr.*, 1899, ii, 1028; from *Arch. Anat. Phys.*, 1899, 552—555. Compare Abstr., 1899, i, 467).—Prepared thymoid glands, after boiling with very dilute acetic acid, are macerated and then boiled with a solution of sodium acetate containing a little sodium hydroxide, the boiling being continued for half an hour if the α -acid is required, and for 2 hours for the β -acid. After neutralising with dilute acetic acid, the liquid is filtered hot, evaporated at 40° to $\frac{1}{2}$ —1 litre, and then treated with an equal volume of alcohol, when the sodium salt separates on cooling. Nucleothymic acid is prepared by dissolving α - or β -nucleic acid in 20 times its weight of water at 60° as quickly as possible, and pouring the solution into 3 times its volume of alcohol containing 15 c.c. of concentrated hydrochloric acid per litre. The precipitate is dissolved in cold water and again precipitated by alcoholic hydrochloric acid solution.

E. W. W.

Thymin. By WALTER JONES (*Zeit. physiol. Chem.*, 1900, 29, 20—23).—Thymin was originally described by Kossel as one of the decomposition products of the nucleic acid of the thymus gland. It has since been obtained from nucleic acid from other sources. Its constitution is not known, although its low percentage of hydrogen possibly indicates a cyclic structure. *Bromothymin*, $C_5H_7O_3N_2Br$, crystallises in long, concentrically-grouped, transparent prisms, and begins to decompose at 130° . Thymin is isomeric, not identical, with methyluracil.

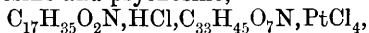
W. D. H.

Reactions of Phrenosin, the Cerebro-galactoside from the Human Brain. By JOHN L. W. THUDICHUM (*J. pr. Chem.*, 1899, [ii], 60, 487—506. Compare Abstr., 1882, 537, and 1896, i, 400).—When phrenosin is triturated with a concentrated aqueous solution of mercuric nitrate, and the product dissolved in strong nitric acid and reprecipitated by the addition of water, a compound is obtained which contains no mercury; it is soluble in ether, and on evaporation of the ethereal solution remains as a hard, snow-white mass, which, on treatment with water, swells and gradually becomes transparent.

A hot alcoholic solution of phrenosin yields with strong aqueous mercuric nitrate, a thick, white precipitate, in which $N : Hg = 3 : 4$. If this substance is washed with dilute nitric acid, a white residue is

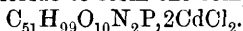
obtained of the composition $C_{41}H_{79}O_8N, 2HgNO_3, 3HgO, 2H_2O$, which is insoluble in alcohol, ether, or benzene; when heated at $85-100^\circ$ in a stream of dry air, it loses water, becomes yellow, and is then soluble in ether.

Sphingosine (Abstr., 1882, 537) melts at $75-80^\circ$, and resolidifies at 70° . It yields the oleocholide reaction in the presence of sucrose. The *nitrate*, $C_{17}H_{35}O_2N, HNO_3$, is a white, crystalline salt, which reacts with mercuric nitrate to form the compounds $C_{17}H_{35}O_2N, HgNO_3$ and $C_{17}H_{35}O_2N, HgO$; on heating the latter with nitric acid, an acid, probably isomeric with palmitic acid, is formed; the *picrate* melts at 75° ; the *platinichloride* forms slender needles. A double platinichloride of sphingosine and psychosine,



crystallises from alcohol in slender needles.

When hydrolysed with baryta, *sphingomyelin*, $C_{58}H_{121}O_{10}N_2P$, does not yield glycerophosphoric acid, but neurine and a "phosphatide" which contains the sphingosyl radicle, are produced. Sphingomyelin reacts with cadmium chloride to form the compound



The paper concludes with a complete list of the products which the author has obtained from phrenosin. E. G.

Seminase, a new Enzyme. By ÉMILE BOURQUELOT and HENRI HÉRISSEY (*Compt. rend.*, 1900, 130, 340—342. Compare this vol., ii, 35).—The enzyme obtained from the seeds of fenu-greek and lucerne rapidly hydrolyses the albumen obtained from carob-tree, but only slowly hydrolyses potato-starch. A parallel experiment made with diastase gave very slow hydrolysis in the former and rapid hydrolysis in the latter case. To this enzyme, which is present in considerable amount in the above seeds, the name *seminase* is given. H. R. LE S.

Precipitation of Zymase from Yeast Extract. By ROBERT ALBERT and EDUARD BUCHNER (*Ber.*, 1900, 33, 266—271).—On pouring yeast extract into twelve times its volume of absolute alcohol or, better, into a mixture of 10 vols. of alcohol and 2 vols. of ether, a flocculent precipitate is obtained containing nearly the whole of the zymase, the activity of the latter not being impaired by drying; with less alcohol, the precipitation is not complete. It appears that the active zymase only constitutes a very small percentage by weight of the precipitate, and redissolves only slowly on stirring with water, having apparently undergone some change under the influence of the alcohol; several hours contact with alcohol diminishes the activity of zymase in a very marked manner. Acetone only partially precipitates zymase from yeast extract. W. A. D.

Organic Chemistry.

Certain Laws and their Application in Organic Chemistry. By ARTHUR MICHAEL (*J. pr. Chem.*, 1899, [ii], 60, 286—384 ; 409—486. Compare Abstr., 1888, 1055, 1056).—An attempt is made to account for various reactions, chiefly of organic compounds, from a single point of view, by considering the sum of the influences exerted upon one another, directly and indirectly, by all the atoms in the molecule. The reactions considered are for the most part the addition and elimination of halogens, hydrogen haloids, and water ; and the substitution of halogens for hydrogen, and of hydroxyl for halogens and *vice versa*. Several reactions have been reinvestigated by improved methods ; namely, the polymerisation of allylene under the influence of sulphuric acid, and the addition of hydrogen iodide, bromine chloride, iodine chloride, and hypochlorous acid to propylene. It was found that a single additive product is seldom, if ever, formed ; the other possible isomeride is also formed, although often in a very small amount. An ingenious method of separating isomeric ketones (into which isomeric halogen derivatives can be converted, through the carbinols) by means of their different behaviour with semicarbazide salts is described. With the dichloroacetate, for instance, 2-pentenone forms a semicarbazone, but 3-pentenone does not ; the latter does, however, with semicarbazide hydrogen phosphate, and so does 2-hexenone, but not 3-hexenone.

The paper is not one that admits of satisfactory abstraction ; reference must be made to the original. C. F. B.

Preparation of Saturated Hydrocarbons. By ALESEI A. WOLKOFF and BORIS N. MENSCHUTKIN (*J. Russ. Phys. Chem. Soc.*, 1899, 31, 1009—1015).—The gases of the paraffin series are readily prepared by adding alcohol (1 mol.), drop by drop, to a mixture of an alkyl iodide (1 mol.) and twice the calculated quantity of powdered magnesium, no extraneous heating being required. This method of preparation, although furnishing a good lecture experiment, yields hydrocarbons containing appreciable quantities of free hydrogen, the proportion of which is largely increased if the alcohol is used in excess ; traces of the alkyl iodide are also present, even after the gas has been passed through a reflux condenser, but are removed by washing with alcohol. Better results are obtained by warming in a water-bath a mixture of equal parts of zinc dust and alkyl iodide, together with a quantity of water equivalent to the iodide taken ; the reaction, which should be carried out in a flask connected with a reflux condenser, begins at 50—60° and is completed at 100°. Thus prepared, the gases contain no free hydrogen, but a small quantity of unsaturated compounds which are entirely removed by means of potassium permanganate either in solution or in the moist state.

T. H. P. ;

b b

Velocity of Formation of Olefines. By S. BRUSSOFF (*J. Russ. Phys. Chem. Soc.*, 1900, 32, 7—28).—A series of experiments has been carried out on the action of alcoholic alkali solutions on alkyl halogen compounds. The alkyl haloid, together with an equivalent quantity of alcoholic potash, was heated in a bath of benzene vapour and the olefine collected in a graduated tube over water; the time taken for each 20 c.c. of gas to collect is regarded as the velocity of the reaction during that time. The proportion of the ether formed along with the olefine is obtained by determining the amount of potash left undecomposed at the end of the reaction. From a preliminary experiment with *isobutyl iodide*, it was found that the curve plotted with the velocities of reaction as ordinates and the total amount of reaction, as measured by the volume of gas evolved, as abscissæ, is not regular unless a certain quantity of potassium iodide is added; this was therefore done in all the following experiments. The curves thus obtained for propyl, *isopropyl*, butyl, *isobutyl*, *sec-butyl*, and *tert-butyl iodides*, and for *isopropyl* and *isobutyl bromides*, rise quickly to a maximum, then fall and finally become straight lines, which theory would indicate them to be. Further, the theoretical maxima of the curves, namely, the points where the rectilinear parts meet the vertical axis, are very nearly identical with the observed maximum velocities of reaction. In the case of *tert-butyl iodide*, considerable deviation from this behaviour occurs, as after rising to a maximum the velocity of reaction remains constant for some time and then falls regularly.

The different alkyl iodides yield very different proportions of olefines; thus, using quantities of the iodides capable of giving 300 c.c. of olefine, the following are the actual volumes obtained: from ethyl iodide, 54 c.c.; propyl iodide, 122 c.c.; *n*-butyl iodide, 117 c.c.; *tert-butyl iodide*, 245 c.c.; *isobutyl iodide*, 265 c.c.; *isopropyl iodide*, 278 c.c.; *sec-butyl iodide*, 290 c.c. Thus the yield of olefine is least with normal iodides and is increased by lengthening the carbon atom chain and also by introducing side-chains. The maximum velocities of reaction for the four butyl iodides have the following relative values: for the normal compound, 1; the *iso*-compound, 2.84; the secondary, 5.06; and the tertiary, 8.00. Hence the velocity of reaction has also its least value for a normal carbon chain and is greater, the greater the number of side-chains present in the molecule; it is further increased if the iodine atom and a side-chain are joined to the same carbon atom. A comparison of the volumes of olefine obtained and of the maximum velocities of reaction when different halogen compounds of the same alkyl group are employed shows that the iodo-compounds are much more suitable than the bromides for the preparation of olefines, whilst the chlorides are quite unsuitable. The replacement of ethyl by methyl alcohol as a solvent makes no difference either in the volume of olefine obtained or in the velocity of reaction in the cases of *iso*- and *sec-butyl iodides*; with the *tert*-iodide, although the same volume of olefine is obtained, yet the maximum velocity of reaction when methyl alcohol is employed is 2.5 times as great as with ethyl alcohol. The use of alcoholic soda instead of potash makes little difference to the volume of gas or to the velocity of reaction.

T. H. P.

Laboratory Method for the Continuous and Uniform Generation of Acetylene, and for its Purification. By JOHN A. MATHEWS (*J. Amer. Chem. Soc.*, 1900, 22, 106—108).—Acetylene is evolved in a steady stream when calcium carbide is covered with absolute alcohol, and water added drop by drop. It may be purified by passing it through a solution of copper sulphate acidified with sulphuric acid, and afterwards over pumice stone saturated with an acetic or sulphuric acid solution of chromic acid. E. G.

Gold Carbide. By JOHN A. MATHEWS and L. L. WATTERS (*J. Amer. Chem. Soc.*, 1900, 22, 108—111).—The yellow explosive precipitate, which Berthelot (*Ann. Chim. Phys.*, 1866, [iv], 9, 425) found to be produced when acetylene is passed into a solution of aurous thiosulphate, is *aurous carbide*, Au_2C_2 . It is decomposed by hydrochloric acid with the formation of acetylene and aurous chloride, and on boiling with water is resolved into its constituent elements.

By the action of acetylene on solution of auric chloride, metallic gold is precipitated, but no precipitate is produced if the solution has been rendered alkaline with potassium hydroxide; solution of potassium auric cyanide also yields no precipitate. E. G.

Action of Amyl Chloride on Calcium Carbide. By P. LEFEBVRE (*Compt. rend.*, 1900, 130, 1036—1039).—The liquid products of the action of amyl chloride on calcium carbide at a dull red heat include β -methyl- Δ^2 -butylene, β -methyl- Δ^4 -butylene, and *sec*-amyl and *tert*-amyl chlorides, whilst the gaseous products consist of hydrogen, acetylene, ethylene, and other hydrocarbons of the ethylene series. The primary reaction is considered to be $\text{CaC}_2 + 2\text{C}_5\text{H}_{11}\text{Cl} = \text{C}_2\text{H}_2 + 2\text{C}_5\text{H}_{10} + \text{CaCl}_2$. N. L.

Compounds of Aluminium Haloid Salts with Organic and Inorganic Substances. II. By MICHAEL I. KONOWALOFF and W. PLOTNIKOFF (*J. Russ. Phys. Chem. Soc.*, 1899, 31, 1020—1027. Compare Abstr., 1899, i, 470).—The molecular weight of the compound $(\text{AlBr}_3, \text{EtBr})_2, \text{CS}_2$ (*loc. cit.*) in boiling ethyl bromide, has for a 6 per cent. solution the value 940.4, and for a 20 per cent. solution 1778, the number required by the formula being 828.

Bromoform and aluminium bromide react in carbon disulphide solution with the formation of the compound, $\text{AlBr}_3, \text{CHBr}_3, \text{CS}_2$, which separates in slender, prismatic, yellow, dichroic crystals which, when heated out of contact with air, melt and partially decompose at 120.7 — 121.3° ; it dissolves slightly in ethyl bromide and more readily in ether. In aqueous solution, it decomposes with the formation of aluminium hydroxide, hydrogen bromide, and *bromomethylene dithiocarbonate*, $\text{CO} \begin{smallmatrix} \text{S} \\ \diagup \diagdown \\ \text{S} \end{smallmatrix} \text{CHBr}$; this compound separates from ether in hard, almost colourless crystals which are soluble in ether or light petroleum, and melt and decompose at 52 — 52.5° .

Ethylidene bromide readily reacts with aluminium bromide in carbon disulphide solution, giving the compound $\text{AlBr}_3, \text{C}_2\text{H}_4\text{Br}_2, \text{CS}_2$, whilst from tribromopropane $\text{AlBr}_3, \text{C}_3\text{H}_5\text{Br}_3, \text{CS}_2$ is obtained.

T. H. P.

Iodide of Cuprous Acetylde. By MARCELLIN P. E. BERTHELOT and MARCEL DELÉPINE (*Ann. Chim. Phys.*, 1900, [vii], 19, 54—56).—The *iodide*, $\text{Cu}_3\text{C}_2\text{I}, \text{CuI}$, of cuprous acetylde is obtained as a bright red precipitate by passing acetylene into a slightly alkaline solution of cuprous iodide in potassium iodide; the quantity of alkali present must not exceed the amount required to combine with the hydrogen iodide set free during the formation of cuprous acetylde, otherwise substances containing more copper, such as $3\text{Cu}_2\text{C}_2, \text{Cu}_2\text{I}_2$ and $\text{Cu}_2\text{C}_2, \text{Cu}_2\text{I}\cdot\text{OH}$, are produced; the latter of these, when dehydrated, yields the compound $(\text{Cu}_2\text{C}_2, \text{Cu}_2\text{I})_2\text{O}$.
G. T. M.

Nitration of Menthane and of Triethylmethane. By MICHAEL I. KONOWALOFF (*J. Russ. Phys. Chem. Soc.*, 1899, 31, 1027—1029).—[With A. JEBENKO].—When menthane is heated at 110° with nitric acid of sp. gr. 1.075, a mixture of *mononitro* compounds, $\text{C}_{10}\text{H}_{19}\text{O}_2\text{N}$, is obtained, about 71 per cent. of the product being tertiary nitro-compound and the rest primary and secondary. When heated with dilute nitric acid, menthane is partially converted into *diisobutyl* and *diisoamyl*.

[With S. KOTSINA].—On nitrating triethylmethane at 120° with nitric acid of sp. gr. 1.075, 57 per cent. of the product consists of the *tert*-nitro-derivative, which boils at $190\text{--}191^\circ$ under 743 mm. pressure, and has a sp. gr. 0.9623 at $0^\circ/0^\circ$ and 0.9471 at $20^\circ/0^\circ$; its molecular refraction (Lorenz and Lorentz formula) is 39.437 at 20° . The remainder (43 per cent.) of the nitrated product, which is a mixture of the primary and secondary nitro-derivatives, boils at $195\text{--}197^\circ$ under 750 mm. pressure, has a sp. gr. 0.9603 at $0^\circ/0^\circ$ and 0.9452 at $20^\circ/0^\circ$; its molecular refraction (Lorenz and Lorentz formula) is 40.065.

T. H. P.

Salts of Nitro-compounds with Nitrated Bases. Separation of Nitro-compounds of Different Types. By MICHAEL I. KONOWALOFF (*J. Russ. Phys. Chem. Soc.*, 1900, 32, 73—75).—The ammonium salts of primary or secondary nitro-compounds are readily obtained by the action of ammonium chloride on the corresponding sodium or potassium compounds. The other method of preparing these salts, namely, by the action of alcoholic ammonia on the nitro-compound, gives good results with *o*-nitrodiphenylmethane, *o*-nitrotoluene, and primary nitromesitylene and nitro-*p*-xylene; the reaction in these cases takes place with development of heat and proceeds to an end, the solid ammonium salt being obtained. With the primary fatty compounds, nitromethane, nitroethane, nitropentane, nitro*diisobutyl* and nitromenthane, very slight action takes place with alcoholic ammonia, whilst no ammonium salt is produced with nitrohexamethylene or β -nitro- γ -ethylpentane, which are secondary nitro-compounds. The action of alcoholic ammonia can hence be used as a method of separating nitro-compounds of different types, as the ammonium salts of these compounds are in general readily soluble in water, and therefore can be easily removed from any nitro-compound not acted on by the ammonia.

Another means of separation of different nitro-compounds is presented by piperidine, which reacts energetically with nitro-compounds

containing a phenyl group to form well-crystallised salts, whilst with other nitro-derivatives, piperidine reacts only slightly or not at all.

Aqueous solutions of the ammonium salts of nitro-compounds are decomposed on the water-bath, ammonia being evolved and the nitro-derivative left behind. On heating the ammonium salt of *o*-nitrodi-phenylmethane at above 150° , water and gases are evolved and a nearly theoretical yield of benzophenone obtained; this may be useful as a general method of converting secondary nitro-compounds into ketones.

T. H. P.

Pentahydric Alcohol from Methylallylcarbinol. By STEPHAN MAXIMOVITSCH (*J. Russ. Phys. Chem. Soc.*, 1900, 32, 61—65).—When methylallylcarbinol is oxidised by gradually adding 1 per cent. potassium permanganate solution, a *pentahydric alcohol* of the constitution $\text{OH} \cdot \text{CMe}[\text{CH}_2 \cdot \text{CH}(\text{OH}) \cdot \text{CH}_2 \cdot \text{OH}]_2$ is obtained; it is a viscid liquid with a sweet taste, and dissolves in water or alcohol, but is almost insoluble in ether. With acetic anhydride, it gives a mixture of a *tetra-acetyl* derivative with a small quantity of the *penta*-compound, the difficulty in completely acetylating being due to the tertiary nature of one of the hydroxyl groups. The mixed acetyl derivative is a colourless, viscous liquid, soluble in water, alcohol, or ether.

T. H. P.

Sulphine and Thetine Derivatives. By DANIEL STRÖMHOLM (*Ber.*, 1900, 33, 823—841. Compare Abstr., 1898, i, 624; this vol., i, 12).—Trimethylsulphine iodide boils slightly above 200° without previously melting, the *picrate* melts at 193° , the *acid tartrate* and the *antimonyl tartrate*, $\text{SMe}_3 \cdot \text{CO}_2 \cdot \text{C}_2\text{H}_4\text{O}_2 \cdot \text{CO}_2(\text{SbO}) + \frac{1}{2}\text{H}_2\text{O}$, form deliquescent plates; the *stannochloride*, $\text{SMe}_3\text{Cl} \cdot \text{SnCl}_2$, melts and decomposes at 216° , and the *lead salt*, $\text{SMe}_3\text{Cl} \cdot \text{PbCl}_2$, crystallises in needles.

Ethyl isopropyl sulphide combines with methyl iodide, at the ordinary temperature, to form *methylethylisopropylsulphine iodide*, $\text{SMeEtPr}^{\text{I}}$, a white, deliquescent substance; the *cadmioiodide*, $2\text{C}_6\text{H}_{15}\text{IS} \cdot \text{CdI}_2$, melts at 166° , and the *platinichloride*, $(\text{SMeEtPr}^{\text{I}})_2\text{PtCl}_6$, forms large, reddish-yellow, orthorhombic crystals, and on heating at 140° loses isopropyl chloride yielding the *compound*, $(\text{SMeEt})_2\text{PtCl}_4$, which melts at 163° . The *stannichloride*, $(\text{C}_6\text{H}_{15}\text{S})_2\text{SnCl}_6$, forms well-defined crystals, and melts and decomposes at 190° .

Methylethylpropylsulphine iodide, $\text{SMeEtPr}^{\text{a}}$, is non-crystalline, but yields a *platinichloride* which forms reddish-yellow, monoclinic crystals [$a : b : c = 1.733 : 1 : 1.712$; $\beta = 81^{\circ}54'$], and decomposes at 140° , without yielding a compound analogous with that derived from the corresponding isopropyl derivative; the *stannichloride* forms lustrous crystals and melts at 220° .

Methylethylbutylsulphine *platinichloride* forms ill-defined crystals; the corresponding *isobutyl* derivative, $(\text{C}_7\text{H}_{17}\text{S})_2\text{PtCl}_6$, forms lustrous, reddish-brown, monoclinic crystals [$a : b : c = 1.0230 : 1 : 0.8880$, $\beta = 83^{\circ}38'$], and the analogous *sec-butyl* compound regular octahedra. Methylethylamylsulphine *platinichloride* forms long prisms, whilst

methylethylhexylsulphine *platinichloride* melts at 124°; the *platinichlorides* of methylethylsecoctylsulphine, methylpropylsulphine, methyl-diisopropylsulphine [rhombohedral crystals, $a:b:c = 1.3500:1:1.3794$], methylpropylisobutylsulphine, methylisopropylisobutylsulphine, methyl-diisobutylsulphine, and methyl-diamylsulphine are also described.

In the interaction of benzyl ethyl sulphide with methyl iodide, partial rearrangement occurs, dimethylethylsulphine iodide being formed as well as benzylmethylsulphine iodide; the *platinichloride* derived from the latter forms small, reddish-yellow needles and melts at 142—144°. Benzylmethylisopropylsulphine *platinichloride* forms sparingly soluble plates and melts at 160°.

A table of solubilities of all the *platinichlorides* described is appended.

The *bromide*, $\text{O:S} \begin{smallmatrix} \text{CH}_2 \cdot \text{CH}_2 \\ \text{CH}_2 \cdot \text{CH}_2 \end{smallmatrix} \text{SMeBr}$, forms white, easily soluble crystals, and melts and decomposes at 181—184°; the *platinichloride*, $(\text{C}_5\text{H}_{11}\text{OS}_2)_2\text{PtCl}_6$, derived therefrom was also prepared. The action of chlorine on oxydiethylenedisulphidemethylsulphine chloride yields the *dichloro*-derivative, $\text{C}_5\text{H}_9\text{OS}_2\text{Cl}_3$, which forms sparingly soluble crystals and decomposes at 167°; the *monochloro*-derivative, $\text{C}_5\text{H}_{10}\text{OS}_2\text{Cl}_2$, is obtained with greater difficulty, and decomposes at 140°.

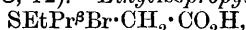
Thetine bromide and bromoacetic acid do not interact in aqueous solution; in the dry state, they yield at 100° a brown, semi-liquid product, insoluble in water. Similar indefinite results were obtained with methyl iodide and thetine bromide, and with bromoacetic acid and diethylenedisulphidemethylsulphine iodide.

Dimethylacetalysulphine iodide, $\text{SMe}_2\text{I} \cdot \text{CH}_2 \cdot \text{CH}(\text{OEt})_2$, cannot be obtained by the interaction of dimethylsulphide with chloroacetal, but is prepared from methylthioacetal, $\text{SMe} \cdot \text{CH}_2 \cdot \text{CH}(\text{OEt})_2$, and methyl iodide; it forms slender, silky crystals, and the *platinichloride*, small, yellow, monoclinic plates [$a:b:c = 1.3110:1:1.6618$; $\beta = 72^\circ 50'$].

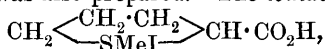
Methylethylacetalysulphine platinichloride,
 $[\text{SMeEt} \cdot \text{CH}_2 \cdot \text{CH}(\text{OEt})_2]_2\text{PtCl}_6$,
 forms large, yellowish-red, monoclinic crystals

[$a:b:c = 1.4438:1:1.6381$; $\beta = 66^\circ 29'$].

Methylethylthetine tartrate could not be obtained crystalline, and attempts to resolve the compound into optically active components by means of ferments and "other methods" failed (compare Pope and Peachey, *Proc.*, 1900, 16, 12). *Ethylisopropylthetine bromide*,



is a white powder, which does not yield a crystalline compound with cinchonine; *ethylisobutylthetine bromide* forms long, thin needles, and melts and decomposes at 109°; *benzylethylthetine platinichloride*, $(\text{C}_{11}\text{H}_{15}\text{O}_2\text{S})_2\text{PtCl}_6$, was also prepared. The *iodide*,



prepared from tetrahydro-2-thiophenecarboxylic acid and methyl iodide, is a white mass, whilst the *thetine*, $\text{C}_6\text{H}_{10}\text{O}_2\text{S} + \text{H}_2\text{O}$, obtained therefrom separates from alcohol in beautiful crystals, and melts at 105°; the corresponding *bromide* forms large, rhombohedral crystals,

and melts at 128° ; the *aurichloride*, $C_6H_{11}O_2SAuCl_4$, decomposes at 170° , and the *platinichloride* forms triclinic crystals

$[a : b : c = 1.309 : 1 : 1.726 ; \alpha = 62^{\circ}33', \beta = 83^{\circ}24', \gamma = 80^{\circ}42']$, and decomposes at 190° .

Vinyl bromide and dimethyl sulphide do not interact. *Ethyl vinyl sulphide*, prepared from ethylsodiummercaptan and vinyl bromide, boils at $90.5-91.5^{\circ}$ (uncorr.), has a sp. gr. 0.887 at 14° , and does not react with methyl iodide at the ordinary temperature; at 50° , dimethylethylsulphine appears to be formed rather than methylethylvinylsulphine.

None of the compounds described containing an asymmetric sulphur atom could be resolved into optically active components by means of *Penicillium glaucum*, or by means of the strychnine or tartaric acid salts; in most cases, the acid tartrates formed non-crystallisable syrups. The thetine salts of the type $CH_2 \begin{smallmatrix} \text{CH}_2 \cdot \text{CH}_2 \\ \text{SMeX} \end{smallmatrix} CO_2H$, which should exist in *cis*- and *trans*-forms, were found to be perfectly homogeneous, whilst no transformation phenomenon was observed in dealing with them.

W. A. D.

Attempts to obtain Optical Antipodes of Quadrivalent Sulphur Derivatives. By L. VANZETTI (*Gazzetta*, 1900, 30, i, 175—186).—*Methylethyl- α -propionothetine bromide*, $SMeEtBr \cdot CHMe \cdot CO_2H$, prepared by the action of α -bromopropionic acid on methyl ethyl sulphide, crystallises in deliquescent, transparent plates. Treatment with freshly precipitated silver chloride yields the corresponding *chloride*, which forms a *platinichloride*, $(C_6H_{12}O_2S)_2, H_2PtCl_6$, separating from water in yellowish-brown, triclinic plates melting and decomposing at $132-133^{\circ}$ $[a : b : c = 0.96547 : 1 : 0.84245 ; \alpha = 82^{\circ}27' ; \beta = 121^{\circ} ; \gamma = 127^{\circ}23']$.

Methylethyl- β -propionothetine bromide, $SMeEtBr \cdot CH_2 \cdot CH_2 \cdot CO_2H$, is obtained as a syrup by the interaction of β -bromopropionic acid and methyl ethyl sulphide in molecular proportion. The *platinichloride*, which separates as a drusy mass of scaly crystals or as microscopic octahedra, melts and decomposes at 164° .

Unsuccessful attempts were made to resolve these thetines by means of *Penicillium glaucum*, *Mucor mucedo*, and *Beggiatoa* (compare Pope and Peachey, *Proc.*, 1900, 16, 12, 43).

T. H. P.

Energy of some Hydroxysulphonic Acids. By F. COJAZZI (*Gazzetta*, 1900, 30, i, 187—188).—The velocities of hydrolysis of methyl acetate by means of hydroxymethane-, hydroxyethane-, and hydroxypentane-sulphonic acids has been measured, and also the electrical conductivities of the sodium salts of these acids. The acids are very strongly dissociated, the value 0.97 being obtained for μ_v/μ_{∞} with dilutions of 256 to 512 litres. Neither Ostwald's, nor van't Hoff's, nor Rudolphi's dissociation formula gives a constant value. The velocities of reaction of the acids are in each case slightly less than the values for the isomeric alkyl hydrogen sulphates.

T. H. P.

Iodation of Fatty Acids. By W. ZERNOFF (*J. Russ. Phys. Chem. Soc.*, 1899, 31, 1029—1033).—By the interaction of *isobutyryl chloride*

(1 mol.), sulphur monochloride ($\frac{1}{2}$ mol.), and iodine, hydrogen chloride is evolved, sulphur deposited, and α -iodoisobutyryl chloride obtained; on hydrolysis, the latter yields α -iodoisobutyric acid, $C_4H_7O_2I$, which separates in large, flat needles, or from a mixture of acetone and light petroleum, in long, well-developed transparent prisms. It melts at 73° and dissolves readily in alcohol, ether, or acetone, and to a less extent in light petroleum or water; it turns brown in 2 or 3 days, even when kept in a desiccator in the dark.

Schützenberger's method (*Compt. rend.*, 1868, i, 1344) of preparing iodoacetic acid, namely, acting on the anhydride of the acid with iodine and iodic acid, was applied to isobutyric acid, but no crystallisable product was obtained.
T. H. P.

β -Methylethylhydracrylic Acid and β -Methylethylacrylic Acid. By ARISTARCH POKROVSKY (*J. Russ. Phys. Chem. Soc.*, 1900, 32, 65—69).— β -Methylethylhydracrylic acid, $OH \cdot CMeEt \cdot CH_2 \cdot CO_2H$, is obtained by oxidising methylethylallylcarbinol with dilute aqueous potassium permanganate as a transparent, syrupy liquid readily soluble in water, alcohol, or ether. Its calcium salt separates in laminæ; the barium salt forms radiating fibrous aggregates, the fibres having approximately straight extinction; the zinc salt, which forms slender, prismatic crystals, and the silver salt are less soluble in water than the preceding salts; the copper and lead salts separate from water in resinous masses, the former slowly crystallising on standing in a desiccator.

β -Methylethylacrylic acid, $CMeEt \cdot CH \cdot CO_2H$, prepared from the hydracrylic acid by dehydration with sulphuric acid, forms a viscous liquid, readily soluble in water, alcohol, or ether; the silver salt separates from water as a flaky precipitate.
T. H. P.

β -Methyl *tert*-Butylhydracrylic Acid. By ZINOVY TALANZEFF (*J. Russ. Phys. Chem. Soc.*, 1900, 32, 69—72).—This acid, which was obtained by Gnedin (*Abstr.*, 1898, i, 291) by oxidising methyl-*tert*-butylallylcarbinol with potassium permanganate, but was not investigated by him, separates, on gently evaporating its ethereal solution, in oblong monoclinic plates melting at 72 — 73° ; angle of extinction, 42° . It dissolves readily in alcohol or ether, but only slightly in water. The sodium and calcium salts both separate from water in dark, badly formed crystals; the magnesium salt is decomposed in aqueous solution, but separates from dilute alcohol, whilst the normal zinc salt could not be prepared; the silver salt crystallises from water in slender needles.
T. H. P.

Action of Caro's Reagent on Ketones. By ADOLF VON BAEYER and VICTOR VILLIGER (*Ber.*, 1900, 33, 858—864. Compare this vol., i, 133 and 206).—When a solution of benzoyl peroxide in ether is treated with an atomic proportion of sodium dissolved in alcohol, the sodium derivative of benzoyl hydrogen peroxide, $COPh \cdot O \cdot ONa$, is precipitated; the substance liberates iodine from potassium iodide, and converts aniline into nitrosobenzene, confirming the authors' opinion that Caro's reagent contains an acid analogous to 'chamber crystals.'

The fact that acetone peroxide prepared by Caro's reagent melts at 132 — 133° , whilst the peroxide prepared by Wolfenstein melts at

94—95° (compare this vol., i, 133), is due to the circumstance that the former substance has a molecular weight corresponding with that required for the formula $(C_3H_6O_2)_2$, the compound of lower melting point having the formula $(C_3H_6O_2)_3$.

When chloroacetone is treated with Caro's reagent, the product consists of an oil and a crystalline substance, which melts at 104—105°, and is indifferent towards potassium iodide; it explodes when struck.

The yield of the lactone of ϵ -hydroxy- $\beta\zeta$ -dimethyloctioic acid from menthone is increased by adding glacial acetic acid to the reagent before the addition of the ketone. The *ethyl* ester of ϵ -hydroxy- $\beta\zeta$ -dimethyloctioic acid, prepared from the lactone and alcoholic sulphuric acid, boils at 152—155° under 15 mm. pressure.

Hydroxymethylhexoic acid, $C_7H_{14}O_3$, is a syrup, forming a crystalline *silver* salt; the *ethyl* ester, produced by the action of Caro's reagent on alcoholic methylcyclohexanone, boils at 141—142·5° under 15 mm. pressure.

Suberone peroxide, $C_7H_{12}O_2$, prepared by adding suberone to a cold mixture of potassium persulphate, alcohol, and the monohydrate of sulphuric acid, crystallises from ether in rhombic leaflets, and melts at 99—100°; it is indifferent towards potassium iodide and boiling caustic soda.

ζ -*Hydroxyheptoic* (*heptane-7-ol-1-oic*) acid, $C_7H_{14}O_3$, is a syrup, forming crystalline *calcium*, *zinc*, *lead*, and *silver* salts; the *ethyl* ester occurs in the filtrate from suberone peroxide, and boils at 146—155° under 15 mm. pressure.

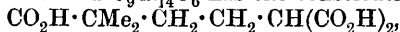
ζ -*Iodoheptoic acid*, $C_7H_{13}O_2I$, obtained on heating the foregoing acid with hydriodic acid, crystallises in lustrous leaflets, and melts at 49—51°.

ζ -*Bromoheptoic acid*, $C_7H_{13}O_2Br$, melts at 30—31°. Potassium permanganate oxidises hydroxyheptoic acid to pimelic acid.

M. O. F.

Constitution of *iso*-Lauronic Acid. By G. BLANC (*Compt. rend.*, 1900, 130, 840—841).—When *isolauronic* acid is reduced with sodium amalgam in alkaline solution, it yields dihydroisolauronic acid, $C_9H_{14}O_3$, which is a γ -ketonic acid and not a β -hydroxy-acid as Perkin has stated (*Trans.*, 1898, 73, 804). When this is oxidised with very dilute sodium hypobromite solution, it yields a new acid, $C_9H_{14}O_6$, which melts at 167—168°, loses carbon dioxide, and is converted into $\alpha\alpha$ -dimethyladipic acid.

It follows that the acid $C_9H_{14}O_6$ has the constitution



whilst dihydroisolauronic acid is $CMe_2 \cdot \begin{smallmatrix} CO-CH_2 \\ CH_2 \cdot CH_2 \end{smallmatrix} \cdot CH \cdot CO_2H$, and

isolauronic acid, $CMe_2 \cdot \begin{smallmatrix} CO-CH \\ CH_2 \cdot CH_2 \end{smallmatrix} \cdot C \cdot CO_2H$ (compare *Abstr.* 1899, i, 925).

C. H. B.

β -Hydroxy- $\alpha\alpha\beta$ -Trimethyladipic Acid. By EDMOND E. BLAISE (*Compt. rend.*, 1900, 130, 1033—1036).—Methyl laevulate condenses with methyl bromoisobutyrate in the presence of zinc to form a compound which, on treatment with dilute sulphuric acid, yields the

methyl ester, $\begin{array}{c} \text{CH}_2 \cdot \text{CH}_2 \\ | \quad \quad | \\ \text{CO} \text{---} \text{O} \end{array} > \text{CMe} \cdot \text{CMe}_2 \cdot \text{CO}_2\text{Me}$, of the lactonic acid corresponding with β -hydroxy- $\alpha\alpha$ -trimethyladipic acid. This is an oily liquid which boils at $162\text{--}165^\circ$ under 19 mm. pressure, and has a sp. gr. 1.1334 at $9^\circ/9^\circ$; it is completely decomposed by alkalis, with the formation of lævulic and isobutyric acids, but when hydrolysed with dilute hydrochloric acid, it furnishes the *lactonic acid*, which crystallises in large prisms melting at $108\text{--}109^\circ$. The *ethyl ester*, which could only be obtained by the interaction of the sodium salt with ethyl iodide, boils at $287\text{--}289^\circ$. When heated to 175° , the lactonic acid loses carbon dioxide, and is converted into a mixture of a *lactone*, $\begin{array}{c} \text{CH}_2 \cdot \text{CH}_2 \\ | \quad \quad | \\ \text{CO} \text{---} \text{O} \end{array} > \text{CMe} \cdot \text{CHMe}_2$, which boils at $234\text{--}236^\circ$ and has a faint odour of camphor, and an unsaturated acid [$\gamma\delta$ -dimethyl- $\Delta\beta$ -hexenoic acid], $\text{CHMe}_2 \cdot \text{CMe} \cdot \text{CH} \cdot \text{CH}_2 \cdot \text{CO}_2\text{H}$, isomeric with the lactone, which boils at $235\text{--}237^\circ$. This acid forms an *ethyl ester* boiling at $203\text{--}204^\circ$, and reacts readily with bromine (2 atoms) to form an additive product which crystallises from benzene in small plates melting and decomposing at $141\text{--}142^\circ$; it also yields a crystalline compound with hydrogen bromide, but when boiled with hydrobromic acid is converted into the isomeric lactone.

N. L.

Alkali Copper Tartrates and Fehling's Solution. II. By FRIEDRICH BULLNHEIMER and E. SEITZ (*Ber.*, 1900, 33, 817—823. Compare Abstr., 1899, i, 868).—Alkali copper tartrates of the type $\text{C}_4\text{H}_2\text{O}_6\text{CuM}'_2$ are obtained by dissolving copper tartrate in an excess of 4 per cent. aqueous alkali hydroxide at a temperature below 50° , or by digesting a solution of the normal alkali tartrate with the calculated quantity of copper hydroxide for 1 hour on the water-bath.

The *sodium copper d-tartrate*, $\text{C}_4\text{H}_2\text{O}_6\text{CuNa}_2 + 2\text{H}_2\text{O}$, forms small, bright blue, lustrous crystals, and dissolves in water with an alkaline reaction; after expelling the water of crystallisation, the salt dissolves in water, giving a *green* solution, which after 2 days becomes blue. The corresponding *sodium copper l-tartrate* has similar properties, and the analogous *racemate* (with $4\text{H}_2\text{O}$) has already been described (Werther, *Annalen*, 1844, 52, 301). Although *potassium* and *lithium copper racemates* (with 3 and $4\text{H}_2\text{O}$ respectively) were prepared, the analogous *d*- and *l*-tartrates could not be obtained, owing to decomposition occurring. Ammonia gives rise either to the tetrammonium tartrates already described (*loc. cit.*), or to a salt which approximates to the formula $\text{C}_4\text{H}_2\text{O}_6\text{Cu}(\text{NH}_3)_2\text{Cu} + 4\text{H}_2\text{O}$.

A third class of salts is obtained by just neutralising a solution of copper tartrate with an alkali carbonate or hydroxide; these salts are bluish-green in solution, cannot be obtained crystalline, and show a great tendency to decompose, although they are not split up by carbon dioxide like the salts of the other two classes (compare also Werther, *Jahresber.*, 1844, 432, and Masson and Steele, *Trans.*, 1899, 75, 725).

Luff has described (*Zeit. ges. Brauw.*, 1898, 21) a *potassium copper citrate*, $\text{C}_6\text{H}_8\text{O}_2\text{Cu}(\text{CO}_2\text{K})_6 + 6\text{H}_2\text{O}$; if the authors' method of preparation of the alkali copper tartrates be applied to citric acid, the *salt*,

$C_6H_8O_2Cu(CO_2K)_6 \cdot OK \cdot C_3H_4(CO_2K)_3 + 12H_2O$, is obtained in beautiful, dark blue crystals.

In the alkali copper tartrates described, it appears that the hydrogen of the original hydroxyl groups of tartaric acid has been replaced by copper, thus $\begin{matrix} CO_2K \cdot CH \cdot O \\ CO_2K \cdot CH \cdot O \end{matrix} > Cu$; in the ditartrates, either the union between the molecules $C_4H_2O_6CuM_2$ and $C_4H_2O_6M_4$ is molecular, or they are combined through the medium of a copper atom, as in the formula $[CO_2Na \cdot CH(ONa) \cdot CH(CO_2Na) \cdot O]_2Cu$.

W. A. D.

Stereoisomeric Forms of Citral. By FERDINAND TIEMANN (*Ber.*, 1900, 33, 877—885. Compare Abstr., 1899, i, 250).—[With MAX KERSCHBAUM.]—The view expressed by Tiemann (*loc. cit.*), according to which ordinary citral consists of two geometrical isomerides, is now confirmed by the isolation of 'citral *b*'; this operation depends on the fact that citral *b*, derived from the semicarbazone which melts at 171° , combines with cyanoacetic acid less rapidly than citral *a*.

Citral *b* has the chemical properties of citral *a*, but it boils at $102\text{--}104^\circ$ under 12 mm. pressure, has a sp. gr. 0.888 at 19° , and the index of refraction 1.49001. The oxime boils at $136\text{--}138^\circ$ under 11 mm. pressure; the β -naphthacinchonic acid melts at 200° .

b-Citralidenecyanoacetic acid crystallises from petroleum in yellowish needles, and melts at $94\text{--}95^\circ$.

The ψ -ionone, prepared from citral *b*, yields a semicarbazone which melts at $143\text{--}144^\circ$, and differing from the derivative of ψ -ionone obtained from citral *a*.

The proportion of citral *b* in lemon grass oil, ordinary citral, and verbena oil has been determined by the cyanoacetic acid method.

M. O. F.

Citronellalacetal. By CARL D. HARRIES (*Ber.*, 1900, 33, 857).—*Citronellal*dimethylacetal, $CMe_2 \cdot CH \cdot CH_2 \cdot CH_2 \cdot CHMe \cdot CH_2 \cdot CH(OMe)_2$, prepared by treating citronellal with a 1 per cent. solution of hydrogen chloride in methyl alcohol (Fischer and Giebe, Abstr., 1898, i, 167), is also produced by the action of methyl iminoformate hydrochloride (Claisen, Abstr., 1898, i, 421). It boils at $110\text{--}112^\circ$ under 12—13 mm. pressure, and has sp. gr. 0.885 at 11.5° .

M. O. F.

Function of Aluminium Chloride in the Friedel-Crafts' Reaction. By GUSTAVE PERRIER (*Ber.*, 1900, 33, 815—816).—The formation of ketones from acid chlorides by means of aluminium chloride takes place in two stages, (1), $2RCOCl + Al_2Cl_6 = (RCOCl)_2 \cdot Al_2Cl_6$; (2), $(RCOCl)_2 \cdot Al_2Cl_6 + C_mH_n = 2HCl + (RCO \cdot C_mH_{n-1})_2 \cdot Al_2Cl_6$, the additive compounds assumed to be formed in these equations being readily isolated in a crystalline form. To obtain the ketones, it is best to prepare the additive compound of the acid chloride and aluminium chloride first, then to add the hydrocarbon, and after the elimination of hydrogen chloride, to decompose the additive compound of the ketone by water.

Analogous additive compounds can be isolated when ferric chloride is used instead of aluminium chloride (compare Nencki, Abstr., 1897, i, 520; 1899, i, 879).

W. A. D.

Electrolytic Oxidation of Ketoximes: New Method of Preparing Aliphatic Nitroso-compounds. By JULIUS SCHMIDT (*Ber.*, 1900, 33, 871—877).—When ketoximes are electrolysed in dilute sulphuric acid solution, they yield pseudonitroles. For instance, acetoxime is converted into propylpseudonitrole, along with an oily compound, $C_3H_6O_4N_2$, which spontaneously undergoes decomposition during the course of a few hours; the oil gives Liebermann's reaction, and is very volatile, the vapour producing extreme irritation in the mucous membrane.

M. O. F.

Rhodoose, a New Sugar of the Methylpentose Series. By EMIL VOTOCEK (*Zeit. Zuck.-Ind. Böhm.*, 1900, 24, 248—257).—By hydrolysing convolvulin with dilute sulphuric acid, a mixture of 1 mol. of glucose with 2 mols. of a new methylpentose, to which the name *rhodoose* is given, is obtained. The glucose can be separated by fermentation, the new sugar being non-fermentable. When prepared from its methylphenylhydrazone, it slowly crystallises in microscopic needles; it is soluble in water and has a specific rotation $[\alpha]_D$ about $+36^\circ$. Its phenylosazone melts at 170° and is soluble in acetone; the diphenylhydrazone, $C_{18}H_{22}O_4N_2$, separates from boiling alcohol in nearly white needles melting at 199° , and is reconverted into rhodoose by the action of benzaldehyde. By means of saturated alcoholic hydrogen chloride, rhodoose is with difficulty converted into a *methylethylpentoside* having a specific rotation $[\alpha]_D$ about $+30^\circ$.

T. H. P.

***d*-Sorbose and *l*-Sorbose (ψ -Tagatose) and their Configuration.** By C. A. LOBRY DE BRUYN and WILLIAM ALBERDA VAN EKENSTEIN (*Rec. Trav. Chim.*, 1900, 19, 1—11).—This paper contains a more detailed account of the purification and physical constants of *l*-sorbose (ψ -tagatose) and its derivatives (compare this vol., i, 208). *Methyl l-sorbose*, prepared by treating *l*-sorbose with methyl alcohol containing hydrogen chloride, melts at 119° and has $[\alpha]_D$ 88.5° .

When reduced with sodium amalgam in a slightly alkaline solution, *d*-sorbose yields *d*-sorbitol and *d*-iditol, which, when treated with benzaldehyde and 50 per cent. sulphuric acid, are converted respectively into dibenzylidene-*d*-sorbitol and tribenzylidene-*d*-iditol; these substances are separated from one another by crystallisation from acetone, in which the latter is only sparingly soluble. *Tribenzylidene-d-sorbitol* is produced when concentrated hydrochloric acid is employed as the condensing agent.

The two alcohols may also be separated by the aid of their methylene derivatives; these compounds are produced by the action of formaldehyde in the presence of concentrated hydrochloric acid. *Trimethylene-d-sorbitol* melts at 202° and has $[\alpha]_D -30^\circ$; *trimethylene-d-iditol* melts at 262° and has $[\alpha]_D -8^\circ$; the latter is very sparingly soluble in alcohol, whereas the former readily dissolves in this medium.

Dibenzylidene-l-sorbitol, obtained from *l*-sorbose, melts at 160° and has $[\alpha]_D -28^\circ$; *tribenzylidene-l-iditol*, which accompanies this substance, is identical with the compound prepared from *l*-idonic acid; *l*-iditol is obtained in a crystalline form by the hydrolysis of its benzylidene derivative.

The *methylene* derivatives of *l*-sorbitol and *l*-iditol are the antipodes

of those of the *d*-series, they melt at 203° and 262° respectively, and have $[\alpha]_D$ 30° and 8°.

G. T. M.

Cryoscopy of Tanret's Rhamninose and Rhamninotriconic Acid. By A. PONSOT (*Bull. Soc. Chim.*, 1900, [iii], 23, 145—147. Compare this vol., i, 78).—The author considers that the conclusions drawn by C. and G. Tanret from their cryoscopic determinations of the molecular weights of rhamninose and of rhamninotriconic acid are not fully justified. In this, as in other similar cases, definite results can only be established by extended series of experiments under different conditions.

N. L.

Solubility of Salts of Calcium, Iron, and Copper in Sucrose Solutions. By F. STOLLE (*Zeit. Ver. Deut. Zuck-Ind.*, 1900, 321—341).—The solubilities of calcium sulphate and sulphide, ferric oxide, ferric hydroxide, triferric tetroxide, ferrous sulphide, and copper sulphide in sucrose solutions of varying concentration were determined at different temperatures. The numbers obtained are given in detail, and lead to the following conclusions: In the case of calcium sulphate, the amount dissolved by a given volume of sugar solution at a fixed temperature decreases as the concentration of the solution increases. Further, at low temperatures (40°), a sugar solution does not dissolve as much calcium sulphate as would the water contained in the solution; at temperatures of about 50—70°, solutions containing up to about 30 per cent. of sugar dissolve more of the salt than their contained water would, whilst with stronger solutions the opposite is the case; at still higher temperatures, the behaviour is similar to that at low temperatures. With calcium sulphide, the solubility increases very quickly with the concentration of the sugar solution and also with the temperature; the solubility curve of any particular solution, like that for water, first falls and then rises as the temperature increases, the temperature of minimum solubility varying with the concentration. Calcium sulphide suffers decomposition when dissolved in sugar solutions. As regards the iron compounds examined, ferric oxide is the only one which gives rise to a sucrate, while with none of them was any invertingaction observable; the solubilities of ferric oxide and hydroxide are extremely small, those of triferric tetroxide and ferrous sulphide somewhat greater, whilst they all give a yellow colour to the solutions. Copper sulphide is very much more soluble in sugar solutions than is ferrous sulphide, and its solubility increases considerably as the temperature rises.

T. H. P.

Action of Silver Oxide and of Hydroxylamine on Bromoamines. By NIC. M. KIJNER (*J. Russ. Phys. Chem. Soc.*, 1899, 31, 1033—1062. See this vol., i, 277).—The action of silver oxide on β -bromoaminohexane yields methyl butyl ketone and β -hexylhydrazine, and on oxidising the latter with alkaline potassium ferricyanide solution, normal hexane is obtained. Similarly, normal heptane and octane are produced by the oxidation of δ -heptylhydrazine and β -octylhydrazine respectively; and 1-bromoamino-3-methylcyclohexane yields with silver oxide the corresponding hydrazine which, with potassium

ferricyanide and alkali, gives methylcyclohexane. When *l*-menthylhydrazine [$\text{Pr}:\text{N}_2\text{H}_3=1:2$] is oxidised in this way, in absence of alkali, it yields a mixture of menthane with a small proportion of menthene; menthane alone is obtained if alkali is present, whilst if the oxidation is carried out in hydrochloric acid solution, menthene and a menthyl chloride are obtained.

The above-described method of preparation of hydrocarbons, namely, the oxidation of hydrazines by means of alkaline potassium ferricyanide solution, offers the advantages that, firstly, all the operations involved are quickly completed, and, secondly, no isomeric change is possible, the structure of the hydrocarbon obtained being hence known when the constitution of the amine employed is known.

The action of the halogen hydracid salts of hydroxylamine on the dibromoamines is partly to convert the latter into the corresponding amines, and partly to form first an intermediate diazo-compound, which is, in its turn, resolved by the halogen hydracid into an unsaturated hydrocarbon on the one hand, and a halogenated hydrocarbon on the other. Thus hydroxylamine hydrochloride with ethyldibromoamine gives ethylene and ethylene dibromide, whilst with *iso*amyl dibromoamine, *iso*amyl bromide is formed. Hydroxylamine hydrobromide and heptyldibromoamine, $(\text{CHPr}^a_2\cdot\text{NBr}_2)$, interact with formation of a heptyl bromide boiling at $155-170^\circ$. With α -methylheptyldibromoamine, hydroxylamine hydrochloride yields α -methylheptylamine, together with a mixture of the corresponding octylene and a bromo-compound. In the case of benzyldibromoamine, no bromotoluene is obtained, as when acted on by hydroxylamine hydrochloride, a mixture of benzyl chloride and bromide is formed, whilst with the hydrobromide it yields benzyll bromide alone.

In alkaline alcoholic solution, the action of hydroxylamine on dibromoamines takes a course differing from that followed in acid solution: the first stage of the reaction gives rise to a hydrazone and a diazo-compound, the latter then decomposing with formation of an alcohol, an unsaturated hydrocarbon, and an ethyl derivative. Thus, in the case of menthyldibromoamine, menthane, menthylhydrazone and diazomenthane are first formed, subsequent decomposition of the diazo-compound yielding menthene, menthol, and the ethyl derivative of menthol, $\text{C}_{10}\text{H}_{19}\cdot\text{OEt}$.

T. H. P.

Acetylation of Primary and Secondary Amines. By L. MUSSELIUS (*J. Russ. Phys. Chem. Soc.*, 1900, 32, 29-35).—The acetates of a number of amines were heated in sealed tubes in a bath of nitrobenzene vapour (212°). The relative velocity of the reaction, which proves to be reversible for both primary and secondary amines, was measured by determining the amount of change produced after half an hour's heating, and the limit of the reaction on prolonged heating was also observed. In the case of methylamine acetate, equilibrium is attained when 80.08 per cent. of the salt is converted into the corresponding substituted amide; this proportion rises as the molecular weight of the primary amine increases, its value for heptylamine being 97.75 per cent. The velocity of reaction also rises with

the molecular weight, being 78.0 per cent. for methylamine and 95.63 per cent. for heptylamine. Both the velocity and limit of reaction for ammonium acetate are intermediate between the corresponding values for the methylamine and ethylamine salts. For secondary amines, the results are given in the following table :

	Velocity of reaction.	Limit of change.
Dimethylamine	84.80 per cent.	92.23 per cent.
Diethylamine	40.74 "	78.32 "
Dipropylamine	51.65 "	84.22 "
Diisobutylamine	41.59 "	82.11 "
Diisoamylamine	50.80 "	84.09 "

It will be seen that the numbers alternately rise and fall as the molecular weight of the amine increases. T. H. P.

Reaction for distinguishing Differently Substituted Amines. By NICOLAI A. MENSCHUTKIN (*J. Russ. Phys. Chem. Soc.*, 1900, 32, 40—41).—The observation of Musselius (preceding abstract) that, when warmed with acetic acid, tertiary amines are not acetylated, whilst primary and secondary are, although at very different speeds, serves as the basis of a method for distinguishing these amines. The amine is sealed up in a glass tube with an equivalent proportion of acetic acid and heated in a bath of nitrobenzene vapour for 30 minutes, after which it is quickly cooled, broken, and the contents mixed with a few c.c. of 96 per cent. alcohol, and titrated with alcoholic potash in presence of phenolphthalein. Primary amines are in general acetylated to the extent of about 87.5 to 95.5 per cent., the proportion for secondary amines being about 40 to 50 per cent. T. H. P.

Influence of the Side-chain on the Properties of Open- and Closed-chain Carbon Compounds. V. Velocity of Combination of Secondary Amines with Alkyl Bromides. By NICOLAI A. MENSCHUTKIN (*J. Russ. Phys. Chem. Soc.*, 1900, 32, 41—45).—In the following table, the mean velocities of combination of allyl bromide with various amines are given.

Ammonia	1380		
Methylamine ..	8302	Dimethylamine ...	30833
Ethylamine	3807	Diethylamine	4952
Propylamine ...	3783	Dipropylamine ...	2910
isoButylamine ...	1240	Diisobutylamine ...	718
isoAmylamine ...	2985	Diisoamylamine ...	1384

The same kind of variation is shown here as was found by Musselius (this vol., i., 334) for the velocities of reaction of the secondary amines with acetic acid. In the case of methylamine and ethylamine, the speed of combination with alkyl bromides is increased by further replacement of the hydrogen of the amino-group, whilst with propyl-, isobutyl- and isoamyl-amines the opposite takes place. This is seen from the following numbers :

$\text{NH}_3 + \text{MeBr} \dots$	5471		
$\text{MeNH}_2 + \text{MeBr} \dots$	31910	$\text{EtNH}_2 + \text{C}_3\text{H}_5\text{Br}$	3807
$\text{Me}_2\text{NH} + \text{MeBr} \dots$	59954	$\text{Et}_2\text{NH} + \text{C}_3\text{H}_5\text{Br}$	4952
$\text{Me}_3\text{N} + \text{MeBr} \dots$	47437	$\text{Et}_3\text{N} + \text{C}_3\text{H}_5\text{Br}$	757
$\text{Pr}^a\text{NH}_2 + \text{C}_3\text{H}_5\text{Br}$	3783	$\text{Pr}^a\text{NH} + \text{C}_3\text{H}_5\text{Br}$	2910
$\text{C}_4\text{H}_9^\beta\text{NH}_2 + \text{C}_3\text{H}_5\text{Br}$	1240	$(\text{C}_4\text{H}_9^\beta)_2\text{NH} + \text{C}_3\text{H}_5\text{Br}$	718
$\text{C}_5\text{H}_{11}^\beta\text{NH}_2 + \text{C}_3\text{H}_5\text{Br}$	2985	$(\text{C}_5\text{H}_{11}^\beta)_2\text{NH} + \text{C}_3\text{H}_5\text{Br}$	1384

T. H. P.

Ethylenetrimethylenediamine and Methylpiperazine. By WERNER ESCH and WILHELM MARCKWALD (*Ber.*, 1900, 33, 761—764. Compare Abstr., 1899, i, 750).—*Ethylenetrimethylenediaminecarbamide*, $\text{NH} \begin{smallmatrix} \text{CH}_2 \\ \text{CH}_2 \end{smallmatrix} \text{N} \cdot \text{CO} \cdot \text{NH}_2$, which separates in tablets on evaporating ethylenetrimethylenediamine hydrochloride with potassium cyanate, crystallises from hot water, and melts at 251° . The *diphenyldithiocarbamide*, $\text{C}_5\text{H}_{10}\text{N}_2(\text{CS} \cdot \text{NHPh})_2$, separates from an alcoholic mixture of the base with 2 mols. phenylthiocarbimide, in glistening, colourless prisms, melts at $216\text{--}217^\circ$, and is only slightly soluble in most solvents. The *thiocarbamate*, $\text{N} \begin{smallmatrix} \text{CH}_2 \text{---} \text{CH}_2 \\ \text{CS} \text{---} \text{S} \\ \text{CH}_2 \cdot \text{CH}_2 \cdot \text{CH}_2 \end{smallmatrix} \text{NH}_2$, separates in white crystals on adding carbon disulphide to an alcoholic solution of the base, and melts and decomposes at 233° . *Diphenylazoethylenetrimethylenediamine*, $\text{C}_5\text{H}_{10}\text{N}_2(\text{N}_2\text{Ph})_2$, separates from alcohol or light petroleum in yellow crystals and melts at 118° .

Di-p-toluenesulphonpropylenediamine,

$\text{C}_7\text{H}_7 \cdot \text{SO}_2 \cdot \text{NH} \cdot \text{CH}_2 \cdot \text{CHMe} \cdot \text{NH} \cdot \text{SO}_2 \cdot \text{C}_7\text{H}_7$, separates from hot alcohol or benzene in white crystals, and melts at $103\text{--}104^\circ$. By heating the sodium salt with ethylene bromide at $130\text{--}140^\circ$, it is converted into *di-p-toluenesulphomethylpiperazide*, $\text{C}_7\text{H}_7 \cdot \text{SO}_2 \cdot \text{N} \begin{smallmatrix} \text{CHMe} \cdot \text{CH}_2 \\ \text{CH}_2 \text{---} \text{CH}_2 \end{smallmatrix} \text{N} \cdot \text{SO}_2 \cdot \text{C}_7\text{H}_7$, which crystallises from hot alcohol and melts at 174° . When hydrolysed with hydrogen chloride, it yields methylpiperazine (Stoehr, Abstr., 1895, i, 569), which can thus be prepared without difficulty. The *aurichloride*, $\text{C}_5\text{N}_2\text{H}_{12} \cdot 2\text{HAuCl}_4$, forms yellow crystals and melts and decomposes at 220° . The *thiocarbamate*, $\text{C}_6\text{H}_{12}\text{N}_2\text{S}_2$, separates in white crystals on adding carbon disulphide to an alcoholic solution of the base, and melts and decomposes at $193\text{--}194^\circ$.

T. M. L.

Dimethylenimine. By WILHELM MARCKWALD (*Ber.*, 1900, 33, 764—766. Compare Abstr., 1899, i, 749; this vol., ii, 149, and Duden and Macintyre, this vol., i, 302).—The author reaffirms his statement that the compound prepared by removing hydrogen bromide from bromoethylamine is not a primary base (vinylamine), but a secondary base (dimethylenimine), and that 'vinylamine' is not yet known. He regards Hinsberg's reaction as more trustworthy than the alkylation method advocated by Duden (this vol., i, 282) for distinguishing primary and secondary bases, since methyl iodide often

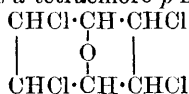
causes opening of the ring in cyclic bases such as those of the pyrrolidine and piperidine series. T. M. L.

Hexethylidenetetramine. By RICHARD KUDERNATSCHEK (*Monatsh.*, 1900, 21, 137—147).—*Hexethylidenetetramine*, $C_{12}H_{24}N_4$, prepared by heating aldehyde-ammonia with 20 per cent. aqueous ammonia in sealed tubes at 140—150°, crystallises from hot water in monoclinic prisms, which contain $6H_2O$ and melt at 96°; when anhydrous, it melts at 102°; it is easily soluble in organic solvents with the exception of chloroform and benzene. It forms an indefinite *additive product* with benzoyl chloride, $C_{12}H_{24}N_4 \cdot 3PhCOCl$, and the unstable *hexabromide*, $C_{12}H_{24}N_4Br_6$, and *tetrabromide*, $C_{12}H_{24}N_4Br_4$. The *hydrochloride*, $C_{12}H_{24}N_4 \cdot 3HCl$, forms colourless, monoclinic prisms, which begin to decompose at 250°, the *platinichloride* decomposes at 200°, and the *hydrobromide* melts and decomposes at 244°. By the action of nitrous acid on hexethylidenetetramine, an undetermined compound, $C_{19}H_{35}O_5N_{11}$, is obtained; it melts and decomposes at 212°, gives the Liebermann reaction, and is decomposed by acids. R. H. P.

Structure of Acid Amides. By NICOLAI A. MENSCHUTKIN (*J. Russ. Phys. Chem. Soc.*, 1900, 32, 35—40).—The author is of opinion that the methods of formation and the reactions of the acid amides accord better with the formula $R \cdot CO \cdot NH_2$ than with the enolic formula $R \cdot C(OH) : NH$. According to the latter formula, in the formation of acetamide from acetic acid and ammonia, and of mono-substituted acetamides by the action of acetic acid on primary amines (see Musselius, this vol., i, 334), the water eliminated is composed of the oxygen atom of the carbonyl group of the acetic acid, and two hydrogen atoms from the ammonia or the amino-group; further, the formation of di-substituted acetamides from acetic acid and secondary amines would require one of the alkyl groups to leave the nitrogen atom and replace the hydrogen of the hydroxyl group. Also the enolic formula for acetyldimethylamide does not give a good explanation of the re-formation of dimethylamine by the taking up of water. The conversion of acetamide derivatives into those of the imino-acids with intermediate formation of nitriles is regarded as due to the fact that the latter are capable of reacting with hydroxy-compounds in the following manner: $R \cdot C : N + H \cdot OR' = R \cdot C(OR') : NH$. T. H. P.

Action of Chlorine Monoxide on Benzene. By ROLAND SCHOLL and WILHELM NÖRRE (*Ber.*, 1900, 33, 723—728).—Chlorine monoxide is readily absorbed by benzene at 0° in the dark. The products of the reaction consist of α - and β -benzene hexachlorides, 2 : 4 : 6-trichlorophenol and a new compound, $C_6H_6OCl_4$. This is an amorphous, white mass, which softens at 60°, melts at 70—75°, and decomposes at about 200°; it is soluble in alcohol, and is decomposed by alcoholic soda and by potassium permanganate, whilst it is not attacked by fuming nitric acid, bromine, acetic anhydride, or phenylhydrazine. On distillation, under diminished pressure, it yields two oils, boiling under the ordinary pressure at 200° and 305—310° respectively, but the nature and

composition of these has not yet been ascertained. It seems probable that the new compound is a tetrachloro-*p*-hexamethylene oxide,



A. H.

Isomorphous Replacement of Halogens and Hydroxyl. By G. FELS (*Zeit. Kryst. Min.*, 1900, 32, 359—417).—Several examples of the isomorphous replacement of fluorine (rarely chlorine) and hydroxyl are known amongst minerals; amongst benzene derivatives, however, the author shows that there is no isomorphous replacement between the halogens (chlorine, bromine and iodine) and hydroxyl. The paper contains detailed crystallographic descriptions of numerous halogen, nitro- and amino-substitution products of benzene and phenol.

L. J. S.

as Iodoso-, *as*-Iodoxy-, and *as*-Iodonium-compounds derived from *m*-Xylene. By CONRAD WILLGERODT and VINCENT ALLEN HOWELLS (*Ber.*, 1900, 33, 841—851).—*m*-Xylene-4-iodochloride, prepared by chlorinating 4-iodo-*m*-xylene in well cooled chloroform and pouring the product into a large quantity of light petroleum, forms stout, yellow needles and melts and decomposes at 91°; it is easily converted by alkalis into the corresponding *iodoso*-compound, the *acetate*, $\text{C}_6\text{H}_3\text{Me}_2 \cdot \text{I}(\text{OAc})_2$, of which crystallises from chloroform in large, white prisms, and melts at 128°. The *basic sulphate*, $[\text{C}_6\text{H}_3\text{Me}_2 \cdot \text{I}(\text{OH})]_2\text{SO}_4$, the first stable sulphate of an *iodoso*-compound which has yet been prepared, forms well defined crystals and melts and decomposes at 113—115°; the *basic nitrate*, $\text{C}_8\text{H}_{10}\text{O}_4\text{NI}$, is a dull yellow, amorphous powder which decomposes at 118°. 4-Iodoxy-*m*-xylene separates from glacial acetic acid as a microcrystalline powder and explodes at 195°.

Di-as-m-xylyliodonium hydroxide, $\text{I}(\text{C}_6\text{H}_3\text{Me}_2)_2 \cdot \text{OH}$, exists only in solution; the *chloride* forms small, white rhombs and melts at 169°; the *bromide*, thick, white needles melting at 170°, whilst the *iodide* forms beautiful, white leaflets and melts at 148°; the *nitrate* is a white, amorphous powder which melts and decomposes at 161°, and the *dichromate*, $(\text{C}_6\text{H}_3\text{Me}_2\text{I})_2\text{Cr}_2\text{O}_7$, an orange mass melting at 145°.

Iododi-as-m-xylyliodonium hydroxide, $\text{C}_6\text{H}_2\text{Me}_2\text{I} \cdot \text{I}(\text{OH}) \cdot \text{C}_6\text{H}_3\text{Me}_2$, prepared by dissolving the *iodoso*-compound in cold concentrated sulphuric acid and subsequently diluting with ice (compare Meyer and Hartmann, *Abstr.*, 1894, i, 242), is strongly alkaline in solution; the *chloride* is a white, amorphous, sparingly soluble substance, which melts at 127—128°, whilst the *bromide* melts at 119°; the *iodide* crystallises in white leaflets and is easily soluble in chloroform, but insoluble in all other solvents; the *dichromate* explodes at 109°.

p-Tolyl-as-m-xylyliodonium hydroxide, $\text{C}_6\text{H}_4\text{Me} \cdot \text{I}(\text{OH}) \cdot \text{C}_6\text{H}_3\text{Me}_2$, yields a *chloride* which crystallises in white needles, and a white, amorphous *mercurichloride*, $(\text{C}_{15}\text{H}_{16}\text{ClI})_2\text{HgCl}_2$; the *bromide* and *iodide* form white needles and melt at 179° and 165° respectively, whilst the *dichromate* is an orange powder.

as-m-Xylyldichloroethyliodonium chloride, $\text{C}_2\text{H}_3\text{Cl}_2 \cdot \text{ICl} \cdot \text{C}_6\text{H}_3\text{Me}_2$, forms stunted, white needles and melts at 171°; the corresponding

bromide and *iodide* form slender needles and melt respectively at 160° and 95°; the *platinichloride* decomposes at 139°. W. A. D.

Preparation of Iodoso- and Iodoxy-compounds. By CONRAD WILLGERODT (*Ber.*, 1900, 33, 853—854).—A controversial paper in which the author reserves for himself certain lines of work.

W. A. D.

Naphthalene Vapour in Coal Gas. By RICHARD W. ALLEN (*J. Soc. Chem. Ind.*, 1900, 19, 209—211).—The author describes experiments which, in his opinion, prove that coal gas containing no appreciable amount of naphthalene vapour still deposits naphthalene in the distributing pipes. It would seem that this must be gradually formed by the action of the hydrocarbon gases on each other in the pipes, but the matter needs further investigation.

L. DE K.

Refraction of Hydrocarbons with Condensed Benzene Nuclei. By ALBERTO CHILESOTTI (*Gazzetta*, 1900, 30, i, 149—169).—Measurements have been made of the refractions of dibenzyl, stilbene, tolane, phenanthrene, retene, and fluorene in benzene solution, and of anthracene in naphthalene solution, the influence of the solvent being allowed for by means of Landolt's formula for mixtures. In the following table, the mean experimental numbers for the molecular refractions are given for the line H_α , together with the values calculated from the structural formula, the atomic refractions used being as follows. For the Gladstone formula: carbon 5, hydrogen 1·30, and a double linking 2·40; for the Lorenz and Lorentz formula: carbon 2·48, hydrogen 1·04, and a double bond 1·78.

	$M \cdot \frac{\mu_{H_\alpha} - 1}{d}$			$M \cdot \frac{\mu_{H_\alpha}^2 - 1}{(\mu_{H_\alpha}^2 + 2)d}$		
	Found.	Calc.	Diff.	Found.	Calc.	Diff.
Dibenzyl.....	103·83	102·60	1·23	59·59	59·96	0·37
Stilbene	115·43	102·40	13·03	65·44	59·66	5·78
Tolane	111·70	99·64	12·06	62·07	58·02	4·05
Anthracene	109·34	97·40	11·94	61·15	55·80	5·35
Phenanthrene.....	110·70	99·80	10·9	61·59	57·58	4·01
Retene.....	145·12	130·2	14·92	80·64	75·82	4·82
Fluorene.....	98·30	92·40	5·90	55·28	53·32	1·96

From these numbers, it is seen that of those given dibenzyl is the only compound which obeys the laws of Landolt and Brühl. The values in the above table differ somewhat from those obtained by Gladstone (this Journal, 1870, 23, 147), the greatest deviation being in the case of anthracene, for which Gladstone found the molecular refraction 100·3.

Taking the centric formula for the benzene nucleus, the refractive value of each centric linking is for naphthalene, anthracene, phenanthrene, and pyrene, 1·39, 1·46, 1·54, and 1·48 respectively, the Gladstone molecular refraction formula being used; with the Lorenz and Lorentz

formula, the value is even more constant, the numbers for each centric linking being for benzene 0.89, naphthalene 0.90, anthracene 0.89, and phenanthrene 0.90. Hence centric structural formulæ for aromatic hydrocarbons accord best with their optical properties.

T. H. P.

Action of Phenylcarbimide and Phenylthiocarbimide on Dibasic Acids. By ÉLOPHE BÉNECH (*Compt. rend.*, 1900, 130, 920—923).—Diphenylmalonamide results from the action of phenylcarbimide on malonic acid, and the corresponding dianilide is obtained in a similar manner from sebacic acid.

The *dianilide* of azelaic acid, produced by heating the acid with phenylcarbimide at 140°, crystallises from methyl alcohol in prismatic needles melting at 185°; it is sparingly soluble in water, benzene, or ether, but dissolves in concentrated nitric acid.

The formation of these anilides is attended by the evolution of carbon dioxide.

Experiments were made with phenylthiocarbimide in order to ascertain whether its action on the dibasic acids is analogous to that of the corresponding carbimide. The reaction follows a similar course in the case of succinic and sebacic acids, the former yielding phenylsuccinimide and the latter its dianilide; carbon oxysulphide is evolved in both cases. Malonic acid, however, when treated with the thiocarbimide, yields diphenylcarbimide and acetanilide, whilst ethylmalonic acid gives rise to butyrylanilide.

G. T. M.

Oxygen Ethers of Carbamides: Methylisocarbamide. By JULIUS STIEGLITZ and RALPH H. MCKEE (*Ber.*, 1900, 33, 807—812. Compare *Abstr.*, 1899, i, 594).—Phenylmethylcyanamide (cyanomethylaniline), obtained from the corresponding thiocarbamide, melts at 30.5°, and not at 28° as stated by Wallach (*Abstr.*, 1899, i, 659). Phenylalkylcyanamides do not combine so readily with ethyl alcohol under the influence of hydrogen chloride as does phenylcyanamide itself; the methyl derivative, for example, requires 14 days, whereas the reaction is complete in the case of phenylcyanamide at the end of 2 days. The addition takes place much more readily in the presence of a small quantity of sodium ethoxide, and is complete at the end of 1 to 2 days. The following generalisation is enunciated: Cyanamides which readily form salts with bases combine most readily with ethyl alcohol under the influence of hydrogen chloride, but cyanamides which are of a more basic character are most readily converted into isocarbamide ethers by the aid of sodium ethoxide.

as-isomer *Phenylmethylethylcarbamide* (ethyl *iminophenylmethylcarbamate*), $\text{NH}_2\text{C}(\text{OEt})\cdot\text{NMePh}$, is a colourless oil distilling at 137° under 21 mm. pressure; its *platinichloride*, $(\text{C}_{10}\text{H}_{14}\text{ON}_2)_2\text{H}_2\text{PtCl}_6$, is brownish-yellow, and melts and decomposes at 160°. When heated at 54° with dry hydrogen chloride, it yields ethyl chloride and as-methylphenylcarbamide. The isomeric as-isomer *phenylmethylethylcarbamide*, $\text{NH}_2\text{C}(\text{OMe})\cdot\text{NEtPh}$, obtained from phenylethylcyanamide, methyl alcohol, and sodium methoxide distils at 126° under 15 mm. pressure.

Methylisocarbamide (methyl *iminocarbamate*), $\text{NH}_2\cdot\text{C}(\text{OMe})\cdot\text{NH}$, is obtained as its *hydrochloride* by the action of dry hydrogen chloride at

0° on silver cyanamide suspended in anhydrous methyl alcohol; it may also be obtained by leaving a solution of cyanamide (1 mol.) and hydrogen chloride ($2\frac{1}{2}$ mols.) in anhydrous methyl alcohol (25 mols.) for 7—14 days, and evaporating to dryness under reduced pressure. After purification by solution in absolute alcohol at 55° and subsequent cooling to -10°, it forms small prisms, melts at 130°, evolving methyl chloride, and is readily soluble in alcohol or water; the *platinichloride*, $(C_2H_6ON_2)_2 \cdot H_2PtCl_6$, forms long, orange-yellow needles, melting and decomposing at 178°. J. J. S.

Influence of the Side Chain on the Properties of Open- and Closed-chain Carbon Compounds. VI. Influence of Chemically Indifferent Solvents on the Comparative Velocity of Reaction in Isomeric Benzene Derivatives. By NICOLAI A. MENSCHUTKIN (*J. Russ. Phys. Chem. Soc.*, 1900, 32, 46—60. Compare Abstr., 1898, i, 186).—In benzene solution, the velocity of reaction of aromatic amines having the amino-group in the side chain with allyl bromide is greater than with methyl bromide, whilst if the amino-group is in the benzene nucleus, the opposite is the case. Using acetone as a solvent, however, no such regularity is observed, as for some compounds with an amino-substituent in the benzene nucleus the velocity constant for combination with allyl bromide is greater than with methyl bromide, for others less, whilst with others again the two are about the same. On the other hand, the velocity constant for the reaction *o*-toluidine + allyl bromide is greater than that for *o*-toluidine + methyl bromide, whether the reaction be carried out in benzene, xylene, bromonaphthalene, acetophenone, *n*-propyl alcohol or methyl alcohol.

The action of allyl bromide on the three toluidines has been studied in various solvents, the results being as follows: In benzene or bromonaphthalene solution, the velocity constant is a maximum for the meta-compound and a minimum for the ortho-base, whilst in acetone, acetophenone, or propyl alcohol, the constant has its greatest value for the para- and its least for the ortho-compound. Similar experiments were carried out for the six xylidines in benzene and acetone.

The acetylation of the three toluidines and the six xylidines was also studied. The speeds of acetylation of the toluidines are decreased in presence of excess of the base, and increased if the acid is in excess.

The conclusion is drawn that chemical reactions taking place in liquid systems of organic compounds proceed in the same way whether an indifferent solvent is present or not. Further, in the case of benzene derivatives, a change in the solvent employed is capable of changing the order of the values of the velocity constants of the reactions of position isomerides. T. H. P.

Action of Formaldehyde on β -Aromatic Hydroxylamines. By EUGEN BAMBERGER (*Ber.*, 1900, 33, 941—955. Compare Abstr., 1894, i, 412).—*Diphenylmethylenedihydroxylamine*, $CH_2(NPh \cdot OH)_2$, formed when concentrated formaldehyde solution (1 mol.) is added to an alcoholic solution of β -phenylhydroxylamine, crystallises in colourless, glistening needles decomposing and melting at 106.5°, and is readily soluble in most organic solvents with the exception of light

petroleum. Its solutions gradually turn yellow owing to its conversion into *N*-phenylglyoxime ether. With ferric chloride, its solutions give a brownish violet-red colour and with alcoholic copper acetate a dark green; most oxidising agents convert it into nitrosobenzene. Other β -aromatic hydroxylamines behave in a similar manner; the products thus formed show feebly acidic and feebly basic properties and are characterised by the readiness with which they undergo decomposition; mineral acids, alkalis, and even boiling water decompose them, yielding hydrogen and *N*-aromatic glyoximes which have an intense yellow colour and are identical with the products obtained by von Pechmann (Abstr., 1898, i, 75) by the action of diazomethane on aromatic nitroso-compounds. It is held to be probable that both diphenylmethylenedihydroxylamine and Pechmann's additive product from diazomethane and nitrosobenzene undergo dissociation into the same products, namely, formaldehyde and phenylimide, which then react to give the same final product, *N*-phenylglyoxime ether.

[With L'ORSA.]—*Di-p-tolylmethylenedihydroxylamine* forms colourless needles melting at 103° and may be recrystallised from a mixture of chloroform and light petroleum. Glyoxime *N-p*-tolyl ether melts at 208° , and when moistened with acetic acid and boiled with dilute sulphuric acid yields toluquinol; with dilute hydrochloric acid, it yields *p*-toluidine and *o*-chloro-*p*-toluidine.

[With FRED. TSCHIRNER.]—*Di-m-tolylmethylenedihydroxylamine* forms glistening needles melting at 118° . *Di-p-chlorophenylmethylenedihydroxylamine* melts at 103° , and after resolidifying melts and decomposes at 140° ; when freshly precipitated, it dissolves readily in mineral acids and is reprecipitated on the rapid addition of acid carbonates; ferric chloride precipitates *p*-chloronitrosobenzene from the sulphuric acid solution, sodium hydroxide yields *di-p*-chloroazoxybenzene. Glyoxime *N-p-chlorophenyl ether* is best obtained by gently warming the finely divided methylene ether with formaldehyde solution, and crystallises from benzene in glistening, golden-yellow plates melting at 239 — 240° .

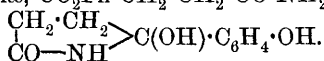
[With ARMAND STIEGELMANN.]—*Di-p-bromophenylmethylenedihydroxylamine* forms glistening needles melting at 95° . Glyoxime *N-p*-bromophenyl ether melts at 230° , whereas von Pechmann (Abstr., 1898, i, 188) gives the melting point as 278° .

[With MARIE BAUM.] — *Di-p-xylyl-O-methylenedihydroxylamine*, $\text{CH}_2(\text{O}\cdot\text{NH}\cdot\text{C}_6\text{H}_3\text{Me}_2)_2$, prepared from 1:4:2-xylylhydroxylamine and formaldehyde, crystallises from a mixture of chloroform and light petroleum in glistening, white needles, melts at 125° , and is readily soluble in benzene or chloroform and in hot alcohol or acetone. It is much more stable than the *N*-ethers described above, and its solutions do not turn yellow; when heated with sulphuric acid, it yields 5-amino-1:4:2-xylenol and with hydrochloric acid, 5-chloro-1:4:2-xylidine, both of which may be regarded as derived from the first products of hydrolysis of xylylhydroxylamine. J. J. S.

Action of Diazomethane on β -Aromatic Hydroxylamines. By EUGEN BAMBERGER and FRED. TSCHIRNER (*Ber.*, 1900, 33, 955—959). —In the expectation of obtaining β -phenylhydroxylamine methyl

ether, the authors have studied the action of diazomethane on β -phenylhydroxylamine; the product formed is, however, the same methylene ether as is obtained by the action of formaldehyde on phenylhydroxylamine (compare preceding abstract), nitrogen and hydrogen being evolved. *m*- and *p*-Tolylhydroxylamines behave in a similar manner, whereas 1:4:2-xylylhydroxylamine yields the corresponding O-ether melting at 125° (compare preceding abstract) together with azoxyxylene melting at 111—111.5°. The authors think that the action of the diazomethane is to be attributed to a dissociation into methylene and nitrogen, a conclusion which is supported by the fact that a polymethylene, $(CH_2)_x$, is usually obtained as a bye-product. It melts at 128° and is insoluble in the usual solvents. J. J. S.

Crystalline Compounds of Succinimide and the Phenols. By M. VAN BREUKELEVEEN (*Rec. Trav. Chim.*, 1900, 19, 32—35).—The compound, $C_6H_6O, C_4H_5O_2N$, produced by heating together equal mols. of succinimide and phenol dissolved in water or benzene, melts at 58—64°, is readily soluble in water or acetone, and insoluble in carbon disulphide or light petroleum; dry ether resolves it into its generators. The constitution of the substance may be expressed by one or other of the following formulæ, $CO_2Ph \cdot CH_2 \cdot CH_2 \cdot CO \cdot NH_2$ or



The corresponding compound from *p*-bromophenol melts at 74—78°; the *p*-cresol derivative melts at 60—70°; the guaiacol compound could not be obtained crystalline.

The germicidal action of the phenol compound is equal to that of the free phenol. G. T. M.

Xylylene Hydrosulphides. By ARTHUR KÖTZ (*Ber.*, 1900, 33, 729—730).—[With SEVIN].—*o*-Xylylenehydrosulphide, which is prepared by the action of alcoholic potassium hydrosulphide on the corresponding bromide, forms white, odourless crystals, melting at 45—46°, and boils at 160° under 20 mm. pressure. *m*-Xylylenehydrosulphide is a thin oil, which boils at 157° under 15 mm. pressure, and has a faint mercaptan-like odour. The *p*-compound is white and crystalline, has a faint aromatic odour, melts at 46—47°, and boils at 156° under 12 mm. pressure. These three compounds are converted by methylene iodide into odourless mercaptals, $C_6H_4 \begin{array}{c} CH_2 \cdot S \\ CH_2 \cdot S \end{array} > CH_2$. *o*-Xylylenemercaptal is a colourless, crystalline substance melting at 152—153°; the *m*-compound is amorphous and melts at 74—75°, and the *p*-compound is also amorphous and melts at 152°. A. H.

Aromatic Esters of Sulphurous Acid. By M. GEORGESCU (*Chem. Centr.*, 1900, i, 543—544; from *Bul. Soc. Sci. Bucuresci*, 8, 668—681).—Aromatic esters of sulphurous acid are readily prepared by the action of benzenesulphonic chloride on alkaline solutions of phenols at the ordinary temperature. The ester, $SO_3Ph \cdot C_6H_4Me$, prepared from *o*-cresol, melts at 39—40°, the *o*-xylyl ester at 72—80°, the *p*-xylyl ester at 51—52°, the guaiacyl ester at 51—52°, the vanillin ester at 68—69°, the methyl salicylate ester, $PhSO_3 \cdot C_6H_4 \cdot CO_2Me$, at

41—42°, the *phenolphthalein ester*, $\text{CO} \langle \text{C}_6\text{H}_4 \rangle \text{C}(\text{SO}_3\text{Ph})_2$, at 112—113°, the *salol ester*, $\text{PhSO}_3 \cdot \text{C}_6\text{H}_4 \cdot \text{CO}_2\text{Ph}$, at 80—82°, and the *salicylaldehyde ester*, $\text{SO}_3\text{Ph} \cdot \text{C}_6\text{H}_4 \cdot \text{COH}$, at 55°. The preceding compounds crystallise from alcohol. The *carvacryl ester* is an oily liquid and decomposes before it distils. The *creosol ester*, $\text{SO}_3\text{Ph} \cdot \text{C}_6\text{H}_3\text{Me} \cdot \text{OMe}$, is a dark yellow oil, and the *eugenol ester* a pale yellow oil. All these compounds are insoluble in water or alkalis, but soluble in organic solvents; they are not attacked by boiling potassium carbonate solution, but are decomposed by boiling with alcoholic potash.

Benzenesulphonic chloride acts on a weak alkaline solution of mononitrophenol as readily as on phenol itself, but the dinitrophenols react less easily, and the trinitrophenols are not attacked. The *o-nitrophenyl ester* crystallises from alcohol and melts at 75°; the *m-nitrophenyl ester* melts at 72—73°, the *p-nitrophenyl ester* at 79—85°, and the *dinitrophenyl ester* at 118°. Only poor yields of these compounds are obtained. The *dinitroresorcinyll ester*, $\text{C}_6\text{H}_2(\text{NO}_2)_2(\text{SO}_3\text{Ph})_2$, melts at 146°, and the *nitronaphthyl ester* forms large, yellow crystals and melts at 117°.

The compound, $\text{SO}_3\text{Ph} \cdot \text{C}_6\text{H}_4 \cdot \text{CO}_2\text{H}$, obtained by the action of benzenesulphonic chloride on salicylic acid, melts at 128—130°, and the compound, $\text{C}_6\text{H}_2(\text{SO}_3\text{Ph})_2 \cdot \text{CO}_2\text{H}$, similarly prepared from gallic acid, crystallises from acetic acid and melts at 200—208°. By the action of benzenesulphonic chloride on *p*-aminophenol, the compounds $\text{SO}_3\text{Ph} \cdot \text{C}_6\text{H}_4 \cdot \text{NH} \cdot \text{SO}_3\text{Ph}$ and $\text{SO}_2\text{Ph} \cdot \text{NH} \cdot \text{C}_6\text{H}_4 \cdot \text{OH}$ are obtained. The former melts at 150—152° and the latter at 125—126°. *o*-Aminophenol yields only the disubstituted product which forms reddish crystals and melts at 81—83°. From diaminophenol, two compounds probably of the composition $\text{SO}_3\text{Ph} \cdot \text{C}_6\text{H}_3(\text{NH} \cdot \text{SO}_2\text{Ph}) \cdot \text{N}(\text{SO}_2\text{Ph})_2$ and $\text{OH} \cdot \text{C}_6\text{H}_3(\text{NH} \cdot \text{SO}_2\text{Ph}) \cdot \text{N}(\text{SO}_2\text{Ph})_2$ respectively are formed. The compound, $\text{SO}_3\text{Ph} \cdot \text{C}_{10}\text{H}_6 \cdot \text{NH}_2$, prepared from β -aminonaphthol, melts at 118—119°.

E. W. W.

Hydrindene and a New Hydroxyhydrindene. By J. MOSCHNER (*Ber.*, 1900, 33, 737—744).—The mother liquors from the crystallisation of pseudocumenesulphonic acid prepared from crude cumene, contain hydrindenesulphonic acid, the sodium salt of which crystallises in well-developed prisms containing $3\text{H}_2\text{O}$. Occasionally, solutions of this salt deposit the needle-shaped, efflorescent crystals containing $4\text{H}_2\text{O}$ which were described by Krämer and Spilker (*Abstr.*, 1891, 205).

When fused with potassium hydroxide, the sodium sulphonate yields *5-hydroxyhydrindene*, $\text{C}_9\text{H}_{10}\text{O}$, which crystallises in white needles melting at 55°, and boils at 255° (corr.). Ferric chloride produces a faint bluish coloration. *5-Methoxyhydrindene*, $\text{C}_9\text{H}_8\text{OMe}$, boils at 233—234° (corr.), and the *ethoxy*-compound at 246° (corr.). The methoxy-compound is converted by oxidation with very dilute nitric acid into 4-methoxyphthalic acid, which on hydrolysis yields 4-hydroxyphthalic acid, the constitution of the hydroxyhydrindene being thus established.

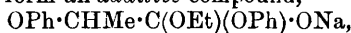
For the sake of comparison, 3- and 4-methoxyphthalic acids were prepared from compounds of known constitution, *3-Methoxy-o-xylene*,

which melts at 29° and boils at 199° (corr.), is converted by oxidation into 3-methoxyphthalic acid, which on hydrolysis yields 3-hydroxyphthalic acid. 3-Ethoxy-o-xylene melts at 10° and boils at 212.5° (corr.). 4-Methoxy-o-xylene boils at $204\text{--}205^{\circ}$ (corr.), and 4-ethoxy-o-xylene at 218° (corr.); the methoxyxylene is converted by oxidation into 4-methoxyphthalic acid.

Sodium hydrindenesulphonate is converted by oxidation with potassium permanganate into 4-sulphophthalic acid, which when fused with potash yields 4-hydroxyphthalic acid, a small amount of hydroxybenzoic acid being formed at the same time. A. H.

Melting Point of Ethyl Formylphenylacetate. By C. G. L. WOLF (*J. Physical Chem.*, 1900, 4, 123—129. Compare Abstr., 1896, i, 552).—By prolonged heating in baths maintained at a constant temperature, the author finds that fusion of ethyl formylphenylacetate will occur at any point above 50° , which is hence the stable triple point. By heating at 100° for some time and then cooling rapidly to -80° , a glassy mass was obtained which liquefied at the ordinary temperature, and deposited crystals of the formyl compound in about 24 hours, so that crystallisation was hastened by the cooling. The probable form of the equilibrium diagram is given. L. M. J.

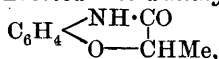
Formation of Chains. XLII. Phenoxypropionic Acids and Derivatives. By CARL A. BISCHOFF (*Ber.*, 1900, 33, 924—931).—Sodium phenoxide condenses with ethyl α -bromopropionate at 160° to form ethyl α -phenoxypropionic acid (Saarbach, Abstr., 1880, 392); neither phenol nor phenetole is produced. α -Phenoxypropionyl-p-phenetide, $\text{OPh}\cdot\text{CHMe}\cdot\text{CO}\cdot\text{NH}\cdot\text{C}_6\text{H}_4\cdot\text{OEt}$, crystallises from alcohol in colourless needles and melts at 119° . Sodium phenoxide and ethyl phenoxypropionate form an additive compound,



which decomposes when heated in a vacuum at 190° .

β -Phenoxypropionic acid, $\text{OPh}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{CO}_2\text{H}$, prepared by the action of sodium phenoxide on β -iodopropionic acid, forms glistening crystals, melts at $97.5\text{--}98^{\circ}$, and does not give acrylic acid when heated. The affinity constant K is 0.0775 for the α - and 0.0054 for the β -acid.

The nitration of α -phenoxypropionic acid gives a mixture of o -nitrophenoxypropionic acid (m. p. $157\text{--}159^{\circ}$) and p -nitrophenoxypropionic acid (m. p. $141\text{--}142^{\circ}$), but these cannot be separated in a pure state by this method. By reduction with iron powder and acetic acid, the ortho-acid is converted into α -methylpheno- β -morpholone,



which separates from boiling water in colourless, glistening crystals and melts at $144\text{--}145^{\circ}$, whilst the para-acid is converted into α - p -aminophenoxypropionic acid, $\text{NH}_2\cdot\text{C}_6\text{H}_4\cdot\text{O}\cdot\text{CHMe}\cdot\text{CO}_2\text{H}$, which crystallises from hot water in needles, and melts at 219° . T. M. L.

Formation of Chains. XLIII. α -Phenoxy-butyric, -isobutyric, and -isovaleric Acids and their Esters. By CARL A. BISCHOFF (*Ber.*, 1900, 33, 931—939).— α -Phenoxybutyric acid (Luchmann, Abstr.,

1896, i, 544) can be prepared by the condensation of ethyl α -bromobutyrate with the theoretical quantity of sodium phenoxide, and hydrolysis of the ester with aqueous potassium hydroxide; it crystallises from light petroleum in eight-sided tablets, melts at $82-83^\circ$ (Luchmann, 96—99°), boils at 258° without any separation of phenol, and has an affinity constant $K=0.0682$.

Ethyl α -phenoxyisobutyrate boils at $160-165^\circ$ under 7 mm. pressure. The acid, $\text{OPh}\cdot\text{CMe}_2\cdot\text{CO}_2\text{H}$, crystallises from dilute alcohol in colourless needles, melts at $97.5-98.2^\circ$, has an affinity constant $K=0.0434$, and is completely decomposed on distillation into phenol and α -methylacrylic acid. On nitration, the chief product appears to be α -o-nitrophenoxyisobutyric acid, and on reducing the crude nitration product with iron powder and acetic acid no *p*-amino-acid could be isolated; the chief product of the reduction is *dimethylphenomorpholone*, $\text{C}_6\text{H}_4\begin{smallmatrix} \text{O}-\text{CMe}_2 \\ | \\ \text{NH}\cdot\text{CO} \end{smallmatrix}$, which crystallises from ether in colourless leaflets and melts at 161.5° .

α -Phenoxyisovaleric acid, $\text{OPh}\cdot\text{CH}(\text{CHMe}_2)\cdot\text{CO}_2\text{H}$, crystallises from light petroleum in long, silky needles, melts at $81.5-82.3^\circ$, has an affinity constant $K=0.0466$, and distils at 250° with formation of a trace of phenol. T. M. L.

Crystalline Form of Indigotin. By P. KLEY (*Rec. Trav. Chim.*, 1900, 19, 12—16).—Crystals of indigotin obtained by sublimation were imbedded in elder pith and cut into sections; microscopic examination of these showed that the crystals belong to the rhombic system, the following faces being commonly exhibited, ∞P , $\infty \bar{P}\infty$, $m\bar{P}\infty$, $m\bar{P}'\infty$. Indigo also separates from boiling aniline solutions in rhombic crystals showing the following faces, ∞P , OP , $\infty \bar{P}\infty$, $m\bar{P}\infty$. The crystals are markedly dichroic and in some cases contain rectangular cavities; the angle of extinction is 0° . Indirubin also crystallises in forms belonging to the rhombic system. G. T. M.

Ethyl Fluoreneoxalate and Indeneoxalate. By WILHELM WISLICHENUS (*Ber.*, 1900, 33, 771—773. Compare Thiele, this vol., i, 298).—

Ethyl fluoreneoxalate, $\text{C}_6\text{H}_4\begin{smallmatrix} \text{C}_6\text{H}_4 \\ > \end{smallmatrix}\text{CH}\cdot\text{CO}\cdot\text{CO}_2\text{Et}$, is prepared by leaving ethyl oxalate in contact with fluorene and sodium ethoxide in benzene solution for several hours at the ordinary temperature, and subsequently decomposing the crystalline sodium derivative with dilute sulphuric acid; it crystallises from benzene on adding light petroleum in lustrous, intensely yellow needles, melts at $74-76^\circ$, and with phenylhydrazine yields initially an *additive* compound, which melts at 125° , decomposes at 140° , and is transformed by crystallisation from glacial acetic acid into the yellow *phenylhydrazone*, $\text{C}_{23}\text{H}_{20}\text{O}_2\text{N}_2$, melting at $150-151^\circ$. *Fluoreneoxalic acid*, $\text{C}_{13}\text{H}_9\cdot\text{CO}\cdot\text{CO}_2\text{H}$, obtained by hydrolysing its ethyl salt, melts, when slowly heated, at $159-160^\circ$.

Ethyl indeneoxalate, $\text{CH}\begin{smallmatrix} \text{C}_6\text{H}_4 \\ < \end{smallmatrix}\text{CH}\begin{smallmatrix} \text{C}_6\text{H}_4 \\ > \end{smallmatrix}\text{CH}\cdot\text{CO}\cdot\text{CO}_2\text{Et}$, prepared in the

same way as ethyl fluoreneoxalate, melts at about 80° , and cannot readily be purified owing to its crystallising with difficulty.

W. A. D.

Condensation Products of Indene and Fluorene. By JOHANNES THIELE (*Ber.*, 1900, 33, 851—853. Compare preceding abstract). — Ethyl indeneoxalate, $\text{CH} \begin{smallmatrix} \text{C}_6\text{H}_4 \\ \text{CH} \end{smallmatrix} \text{CH} \cdot \text{CO} \cdot \text{CO}_2\text{Et}$ or

$\text{CH} \begin{smallmatrix} \text{C}_6\text{H}_4 \\ \text{CH} \end{smallmatrix} \text{C} : \text{C}(\text{OH}) \cdot \text{CO}_2\text{Et}$, crystallises from light petroleum in orange-red needles and melts at 85° . From the mother liquors of the compound melting at 135° , obtained by Marckwald (*Abstr.*, 1895, i, 535) from the interaction of indene with benzaldehyde, a compound can be isolated, which forms orange-red, nodular crystals, melts at 87° , and is possibly benzylideneindene. *Benzylidenefluorene* (*phenyl*

diphenylene-ethylene), $\begin{smallmatrix} \text{C}_6\text{H}_4 \\ \text{C}_6\text{H}_4 \end{smallmatrix} \text{C} : \text{CHPh}$, obtained by the sodium ethoxide condensation of benzaldehyde with fluorene in alcoholic solution, crystallises from alcohol in lustrous, white leaflets and melts at 76° .

W. A. D.

Condensation of Benzyl Cyanide and Ethyl Fumarate. By MARTIN HENZE (*Ber.*, 1900, 33, 966—971). — Ethyl fumarate (1 mol.) is added to a mixture of benzyl cyanide (2 mols.), sodium ethoxide (2 mols.), and absolute alcohol, and the whole warmed for 1—2 hours on the water-bath; the crude product is warmed with excess of sodium carbonate solution for some time on the water-bath, and when cold a *monosodium* salt separates as a sparingly soluble powder, which crystallises from water in glistening plates or needles. When treated with dilute sodium hydroxide, it dissolves, but in a few minutes crystals of a *disodium* salt are deposited; this separates from alcohol in colourless needles and is much more readily soluble in water than the monosodium salt. Carbon dioxide precipitates the monosodium salt from aqueous solution of the disodium salt and dilute mineral acids precipitate a *lactone*, melting at 204 — 205° , for which the constitution $\text{O} \begin{smallmatrix} \text{CO}-\text{CH}_2 \\ \text{CPh}(\text{CN}) \end{smallmatrix} \text{CH} \cdot \text{CO} \cdot \text{CHPh} \cdot \text{CN}$, is suggested; this is readily soluble in most organic solvents with the exception of ether and light petroleum. The *methyl* ester, obtained by heating the monosodium salt with methyl alcohol and methyl iodide, crystallises in glistening plates melting at 156° , and is readily hydrolysed by sodium hydroxide or carbonate. The *oxime* crystallises in needles, melts and decomposes at 179 — 180° , and although the compound contains a nitrile group, is not to be regarded as an amidoxime.

An acid which softens at 105° and is completely fused at 115° has also been isolated from the original condensation product. J. J. S.

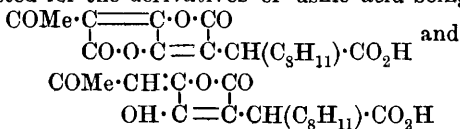
Usnic Acid. By OSKAR WIDMAN (*Annalen*, 1900, 310, 265—301. Compare this vol., i, 235). — Decarbusnic acid is the name by which Paterno originally indicated the compound $\text{C}_{17}\text{H}_{18}\text{O}_6$, obtained when usnic acid, $\text{C}_{18}\text{H}_{16}\text{O}_7$, is heated with alcohol at 150° ; the discoverer subsequently referred to this substance as decarbusnein (Paterno,

Abstr., 1882, 1080), but the present author points out that the original name is more suitable. The acid is optically inactive, and is dibasic; it crystallises from alcohol in long, yellowish needles, and melts at 176—177°. Alkaline solutions become red, and finally brown, when exposed to air, and reduce alkaline solutions of copper and silver salts when heated; potassium permanganate oxidises the substance instantaneously. The acetyl derivative, $C_{17}H_{17}O_5 \cdot OAc$, crystallises from methyl alcohol in small needles and melts at 120—121° (compare Hesse, Abstr., 1895, i, 299); an alcoholic solution develops a dark brownish-red coloration with ferric chloride. The *oxime anhydride*, $C_{17}H_{17}O_5N$, obtained by heating decarbusnic acid with a solution of hydroxylamine acetate in alcohol, crystallises in long, white, slender needles and melts at 214°; it dissolves readily in cold sodium hydroxide, becoming green, and finally dark brown, when exposed to air, the alcoholic solution developing a greenish-black coloration with ferric chloride. The *acetyl* derivative, $C_{19}H_{19}O_6N$, prepared by the action of boiling acetic anhydride on the oxime anhydride, crystallises from methyl alcohol in small, colourless needles which melt at 142°; it is insoluble in cold sodium hydroxide, and develops a green coloration when the alcoholic solution is treated with ferric chloride. The *phenylhydrazine* derivative, $C_{29}H_{28}O_3N_4$, prepared from alcoholic decarbusnic acid, phenylhydrazine, and acetic acid, crystallises in minute leaflets and melts at 210°; the production of this substance, which is insoluble in cold aqueous potash, involves addition of 2 mols. of phenylhydrazine with elimination of 3 mols. of water. The *compound*, $C_{17}H_{20}O_5N_2$, obtained on heating an alcoholic solution of decarbusnic acid with semicarbazide hydrochloride, melts at 237°, and becomes black when the solution in alcohol is treated with ferric chloride. The *anilide*, $C_{23}H_{23}O_5N$, crystallises from alcohol in long, slender, white needles, and melts at 235°; it dissolves slowly in cold potassium hydroxide.

iso-Decarbusnic acid, $C_{17}H_{18}O_6$, occurring as a bye-product in the preparation of decarbusnic acid, crystallises from alcohol in flat needles and melts at 197°; it is optically inactive, and the alcoholic solution becomes violet black when treated with ferric chloride. The acid dissolves very readily in sodium hydroxide, forming a yellow solution which darkens when exposed to air; potassium permanganate oxidises the liquid immediately.

Usnic acid, $C_{18}H_{16}O_8$, a dibasic acid obtained by incompletely oxidising usnic acid with potassium permanganate, crystallises from glacial acetic acid in yellow, rhomboidal plates, which become red at about 166°, and subsequently decompose and evolve gas; the alcoholic solution develops a brown coloration with ferric chloride, and solutions of the alkali salts are yellow or reddish-yellow. The acid is very unstable, and crystalline derivatives have not yet been obtained.

A theoretical discussion brings the paper to a conclusion, the formulæ suggested for the derivatives of usnic acid being based on the expressions



for usnic and decarbusnic acids respectively.

M. O. F.

Attempts to obtain Active Isomerides of Hexahydro- and Isohexahydromellitic Acids. By PIO DE STEFANI (*Gazzetta*, 1900, 30, i, 187).—Hexahydromellitic acid, which is regarded by the author as a possible racemic compound, is not resolved into optically active components by either *Penicillium glaucum* or *Aspergillus glaucus*, nor is isohexahydromellitic acid acted on by *Penicillium* or *Mucor mucedo*.

T. H. P.

Friedel and Crafts' Reaction. By J. BOESEKEN (*Rec. Trav. Chim.*, 1900, 19, 19—26).—In the synthesis of aromatic ketones and sulphones by means of Friedel and Crafts' reaction, the condensation takes place in three stages: (1) $R \cdot COCl + AlCl_3 = R \cdot COCl, AlCl_3$; (2) $R \cdot COCl, AlCl_3 + HR' = R \cdot COR', AlCl_3 + HCl$; (3) $R \cdot COR', AlCl_3 + nH_2O = R \cdot COR' + AlCl_3 \cdot nH_2O$, where HR' represents an aromatic hydrocarbon or one of its derivatives (compare Perrier, this vol., i, 331).

Compounds of the type $R \cdot COCl, AlCl_3$ have been obtained with benzoyl chloride, its *m*- and *p*-nitro-derivatives, and benzenesulphonic chloride. When these substances are treated with benzene, toluene, or anisole, compounds of the type $R \cdot COR', AlCl_3$ are produced; the following are described: $COPh_2, AlCl_3$, $COPh \cdot C_6H_4Me, AlCl_3$, $COPh \cdot C_6H_4 \cdot OMe, AlCl_3$ and the corresponding *m*- and *p*-nitro-derivatives, $NO_2 \cdot C_6H_4 \cdot COR, AlCl_3$, $SO_2Ph_2, AlCl_3$, $SO_2Ph \cdot C_6H_4Me, AlCl_3$, and $SO_2Ph \cdot C_6H_4 \cdot OMe, AlCl_3$. By boiling these compounds of the second type with 80 per cent. alcohol, the ketones and sulphones are obtained in a state of purity.

The sulphone, $SO_2Ph \cdot C_6H_4 \cdot OMe$, melts at 81°.

G. T. M.

Alkylation of Ketones. By JOHN U. NEF (*Annalen*, 1900, 310, 316—335. Compare this vol., i, 4).—The author's explanation of the mechanism of such changes as the methylation of ammonia, ethyl sodiomalonate, and the cyanides, involves the assumption that the alkyl haloid undergoes dissociation into halogen hydride and a substituted methylene, which is then added to the substance under treatment (compare *loc. cit.*); the production of ethers during the action depends on the presence of an alcohol, and the preponderance of ether-formation over the first-named change is a question of the relative powers of dissociation displayed by the two competing substances. In presence of alcohol, ketones are indifferent towards alkyl haloids, but the author has found that when heated with methyl iodide and powdered potassium hydroxide, ketones readily undergo methylation. Acetophenone, for instance, yields phenyl ethyl ketone, phenyl *iso*-propyl ketone, and phenyl *tert*-butyl ketone, whilst phenyl ethyl ketone gives rise to phenyl *isopropyl* ketone.

Attempts to methylate phenyl *tert*-butyl ketone were fruitless, because the action of potash at 160° during 10 hours resolves the substance into benzene and trimethylacetic acid; the *oxime* crystallises from alcohol in flat, lustrous needles melting at 165°, and the *phenyl-hydrazone* crystallises in colourless needles and melts at 92°.

Dibenzylacetophenone, $COPh \cdot CH(CH_2Ph)_2$, prepared by heating acetophenone with benzyl chloride and potassium hydroxide at 160—170°, crystallises in colourless needles melting at 78°, and boils at 240—250° under 18 mm. pressure.

Methylation of acetone under the conditions described gives rise to

methyl ethyl ketone, methyl isopropyl ketone, diethyl ketone, and a small proportion of ethyl isopropyl ketone; further action of methyl iodide on these compounds yields methyl *tert*-butyl ketone (pinacolone) and diisopropyl ketone. *iso-Propyl butyl ketone* (pentamethylacetone), $\text{COPr}^i\text{CMe}_3$, prepared by heating pinacolone with methyl iodide and potassium hydroxide at $130\text{--}140^\circ$, boils at 134° . The *oxime* crystallises from dilute alcohol in lustrous leaflets melting at 140° , and is extremely volatile; the isomeric *amide*, which melts at 115° , is the result of a Beckmann transformation.

Phenylmethylacetylene, CPh^iCMe , obtained by heating phenylacetylene with methyl iodide and potassium hydroxide, boils at $74\text{--}75^\circ$ under 14 mm. pressure, and at $181\text{--}182^\circ$ under atmospheric pressure.

The decomposition of the calcium salts of certain aliphatic acids on distillation is discussed from the point of view of the author's dissociation hypothesis.
M. O. F.

Ketoximes. By PAVEL IW. PETRENKO-KRITSCHENKO and P. KASANEZKY (*Ber.*, 1900, 33, 854—856. Compare Abstr., 1899, i, 706).—Other oximes besides the one already investigated (*loc. cit.*) form double compounds with certain solvents.

β -Benzildioxime crystallises with ethylene glycol ($1\frac{1}{2}$ mols.), glycerol ($\frac{1}{2}$ mol.), benzene (1 mol.), acetic acid ($1\frac{1}{2}$ mols.), aniline (2 mols.), pyridine (2 mols.), and acetone (1 mol.).

The oxime of ketohydroxytriphenyltetrahydrobenzene (Smith, Abstr., 1893, i, 219) crystallises with alcohol (1 mol.), glycerol ($1\frac{1}{2}$ mols.), acetic acid (3 mols.), aniline (2 mols.), and acetone (3 mols.).

Diacetyldioxime crystallises with pyridine (2 mols.) and ethylene glycol ($\frac{1}{2}$ mol.).

The double compounds with organic substances having a high boiling point usually melt at a lower temperature than the oxime itself; the derivatives of more volatile liquids dissociate before the melting point of the oxime is reached.
M. O. F.

Anthraphenones. By GUSTAVE PERRIER (*Ber.*, 1900, 33, 816).—In addition to the anthraphenone melting at 143° (Lippmann and Fleissner, Abstr., 1899, i, 918, give 138°), obtained by the action of benzoyl chloride on anthracene in presence of aluminium chloride, an isomeride crystallising in white, lustrous needles and melting at 75° is also formed (compare *Thesis*, Paris, 1896), together with a third isomeride which forms small, white plates and melts at 203° .

W. A. D.

Action of Menthol on Ethyl Acetoacetate. By PAUL COHN (*Monatsh.*, 1900, 21, 200—204).—Menthol and ethyl acetoacetate, when heated at $140\text{--}150^\circ$ for 4 hours, condense with the formation of *menthyl acetoacetate*, which crystallises in needles melting at $30\text{--}32^\circ$, boils at 145° under 11 mm. pressure, and has a specific rotation $[\alpha]_D - 56\cdot60^\circ$. It yields a *phenylhydrazide*, $\text{N}_2\text{HPh}\cdot\text{CMe}\cdot\text{CH}\cdot\text{CO}_2\cdot\text{C}_{10}\text{H}_{19}$, which forms yellowish crystals melting between 81° and 83° .

R. H. P.

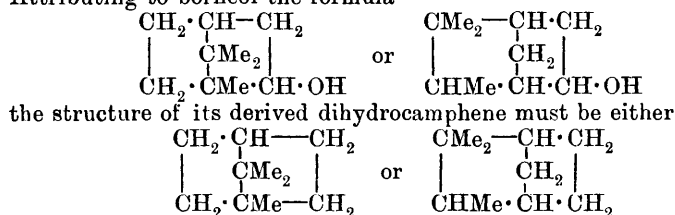
Menthyl Acetoacetate. By PAUL COHN and SIEGFRIED TAUSCH (*Ber.*, 1900, 33, 731—734. Compare preceding abstract).—Menthyl

acetoacetate readily yields a phenylhydrazide, which crystallises in monoclinic tablets melting at $82-83^{\circ}$ and decomposes spontaneously after a few days. Both menthyl acetoacetate and the hydrazide have a similar physiological action to menthol itself, whilst neither of them is a strong antiseptic. Menthyl acetoacetate readily yields a *cyanhydrin*, $C_{15}H_{25}O_3N$, which crystallises, with $1H_2O$, in lustrous needles. The *sodium* salt of the ester is a white, deliquescent mass, which readily reacts with alkyl iodides, but does not yield pure products.

A. H.

Borneol and iso-Borneol. By FRIEDRICH W. SEMMLER (*Ber.*, 1900, 33, 774—778).—*iso*-Borneol, on being heated with zinc dust for half an hour at 220° , yields a small quantity of camphene together with a larger proportion of a *dihydrocamphene* (*isodihydrocamphene*), $C_{10}H_{18}$, which crystallises from alcohol in fern-like aggregates belonging to the cubic system, melts at 85° and boils at 162° (uncorr.); borneol under similar conditions remains unchanged. It thus appears that *isoborneol* is a tertiary and borneol a secondary alcohol, since zinc dust is only capable of removing oxygen from tertiary alcohols (*Abstr.*, 1894, i, 611); the view that borneol and *isoborneol* are stereoisomerides must thus be rejected (compare Biltz, *Abstr.*, 1899, i, 297; Wagner, *Chem. Zeit.*, 1899, 930).

Pinene hydrochloride, which is now known to be the true chloride corresponding with borneol (compare Wagner and Brickner, this vol., i, 46), when reduced with sodium and alcohol, yields a *dihydrocamphene*, $C_{10}H_{18}$, which separates from alcohol in crystals belonging to the hexagonal system, melts at 155° and boils at $160-162^{\circ}$ (uncorr.). Attributing to borneol the formula



W. A. D.

New Terpenoid Alcohol and its Derivatives. By P. GENVRESSE (*Compt. rend.*, 1900, 130, 918—920).—*Pinenol*, $C_{10}H_{16}O$, obtained by passing nitrous fumes into cooled pinene, distilling the product in steam, and fractionating the distillate under ordinary and reduced pressures, is a pale yellow liquid having an agreeable odour; it boils at 225° under 740 mm., and at 143° under 38 mm. pressure; it has a sp. gr. 0.9952 at 0° , and index of refraction 1.497; its molecular refraction is 44.563; the theoretical value calculated from Bruhl's data is 44.85, assuming the presence of one double linking in the molecule. The alcohol is insoluble in water but miscible in all proportions with the ordinary organic solvents; in chloroform solutions, it has $[\alpha]_D -14.66^{\circ}$. When distilled under ordinary pressures, pinenol is partly decomposed; it yields cymene on treatment with phosphoric oxide and combines with 1 mol. of bromine.

The *acetate* boils at 150° under 40 mm. pressure and has an odour resembling that of lavender.

Pinenone, $C_{10}H_{14}O$, resulting from the oxidation of pinenol with chromic acid mixture at the ordinary temperature, is a yellow liquid having an agreeable odour and boiling at 132° under 42 mm. pressure, it has a sp. gr. 0.9953 at 0° , $[\alpha]_D$ in chloroform solution -21.12° , and an index of refraction 1.5002; its molecular refraction is 44.33, the calculated value, assuming the existence of one double linking, being 43.84. The ketone is insoluble in water but miscible in all proportions with the ordinary organic solvents; it combines with 1 mol. of bromine, and yields a *semicarbazone* melting at 82° .

Pinenonoxime, $C_{10}H_{14}:NOH$, is prepared by heating the ketone with an alcoholic solution of hydroxylamine; a small quantity is also formed in the preparation of pinenol from pinene; in this experiment, it is, however, formed from pinenone, and not from the alcohol, since the latter does not yield the oxime on treatment with nitrous fumes. The compound crystallises in the orthorhombic system, melts at 89° , distils with partial decomposition at 170° under 40 mm. pressure, and has $[\alpha]_D -22.3^{\circ}$. It combines with bromine (1 mol.), forming the *dibromide*, $C_{10}H_{14}Br_2:NOH$, melting at 152° ; the *phenyl carbimide*, $C_{10}H_{14}\cdot NO\cdot CO\cdot NHPh$, crystallises in needles melting at 135° ; the *benzoyl* derivative, $C_{10}H_{14}:NOBz$, crystallises from alcohol and melts at 105° , and the *butyryl* derivative melts at 74° . G. T. M.

Conversion of Carvone into Limonene. By L. TSCHÜGAEFF (*Ber.*, 1900, 33, 735—736).—Dihydrocarveol, prepared by the reduction of *d*-carvone, can readily be converted by the method previously described by the author (this vol., i, 129) into *methyl dihydrocarvylxanthate*, $C_{10}H_{17}\cdot O\cdot CS_2Me$, which is a thick, yellow oil. On distillation, this substance yields two hydrocarbons, one boiling at $172-173.5^{\circ}$, and the other at $174-176^{\circ}$. With bromine, the latter yields limonene tetrabromide, which, by the action of zinc dust on the alcoholic solution, is converted into pure *d*-limonene. The hydrocarbon of lower boiling point is more strongly dextrorotatory than limonene, and appears not to yield a crystalline tetrabromide; its nature is being investigated. A. H.

Preparation of Camphene and Menthene from the Corresponding Alcohols. By MICHAEL I. KONOWALOFF (*J. Russ. Phys. Chem. Soc.*, 1900, 32, 76—77).—Camphene is readily obtained from borneol by heating with sulphuric acid, diluted with double its volume of water, at a temperature of $60-100^{\circ}$ for 6 to 8 hours; in the same way, menthene may be prepared from menthol. The yield of hydrocarbon is in each case about 90 per cent. of the theoretical. This method may be used for obtaining other hydrocarbons, and also for preparing methylcyclohexamethylene ketone from pulegone.

T. H. P.

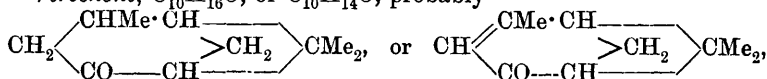
Essence of Chrysanthemum. By GUSTAVE PERRIER (*Bull. Soc. Chim.*, 1900, [iii], 23, 216—217).—The green leaves of *Chrysanthemum Japonicum*, when distilled with water, yield about 0.16 per cent. of a greenish, somewhat oily liquid, having an odour recalling

mint and camomile, which boils at 160° , and has a sp. gr. 0.932 at 15° and refractive index 1.4931 at 18° . It is almost insoluble in 70 per cent., but soluble in 10 parts of 95 per cent., alcohol; when cooled to -15° , it deposits a small quantity of an amorphous solid, probably a paraffin, and at a still lower temperature it completely solidifies. The essence has an acid reaction, partially combines with sodium hydrogen sulphite, and has a saponification number 8.61; the products of hydrolysis seem to include angelic acid. N. L.

The Aldehydic Constituents of Oil of Verbena. Verbenone. By MAX KERSCHBAUM (*Ber.*, 1900, 33, 885—893).—A sample of oil of verbenone, of sp. gr. 0.903 at 17° , and having $\alpha_D -12^{\circ}30'$, obtained from Grasse, was found to contain 26 per cent. of citral and 74 of terpenes and alcohols; the citral contained 17—20 per cent. of citral *b* in addition to citral *a* (compare Tiemann, *Abstr.*, 1899, i, 250). No transformation of the citral takes place, as Barbier supposes (*Abstr.*, 1899, i, 769), when it is converted into the hydrosulphonic acid.

Another sample, of Spanish origin, had a sp. gr. 0.926 at 17° , and $\alpha_D +2^{\circ}45'$. This was shaken with aqueous sodium sulphite and hydrogen carbonate, the solution extracted repeatedly with ether, and then decomposed with sodium hydroxide. The regenerated aldehyde, &c., was shaken with alkaline cyanoacetic acid solution until it dissolved, and the solution extracted repeatedly with ether. The product so obtained is a ketone, and has been named *verbenone*. The oil contained 13 per cent. of citral, 1 of verbenone, and 86 of alcohols and terpenes; the citral contained 18—20 per cent. of citral *b*.

Verbenone, $C_{10}H_{16}O$, or $C_{10}H_{14}O$, probably



is a colourless oil with an odour suggestive of camphor and peppermint; it boils at 103 — 104° under 16 mm. pressure, has a sp. gr. 0.974 at 17° , index of refraction n_D 1.49951, and rotation $\alpha_D +66^{\circ}$; its *semicarbazone* melts at 208 — 209° . It decolorises permanganate at once, but not bromine in acetic acid solution; it is not affected by alkalis, and does not condense with acetone. When oxidised with permanganate, at 0° , at starting it yields a very little acetone, but the main product

is a *ketonic acid*, $C_9H_{14}O_3$, probably $\text{CO}_2\text{H} \cdot \text{CH} \begin{array}{c} \diagup \text{CMe}_2 \\ \diagdown \text{CH}_2 \end{array} \text{CH} \cdot \text{COMe}$,

which melts at 127 — 128° , does not decolorise bromine, and decolorises permanganate only when heated; its *semicarbazone* melts at 212° . When treated with alkaline hypobromite, this acid yields bromoform and an acid, $C_8H_{12}O_4$, identical with Baeyer's norpic acid (*Abstr.*, 1896, i, 621); when evaporated with acetyl chloride and then heated with aniline, it yields an *anilic acid*, $C_{14}H_{17}O_3N$, which melts at 212 — 213° . C. F. B.

India-rubber. By CARL OTTO WEBER (*Ber.*, 1900, 33, 779—796, and *J. Soc. Chem. Ind.*, 1900, 19, 215—221).—In agreement with Gladstone and Hibbert (*Trans.*, 1888, 53, 679), the author finds that

Para rubber contains but a small quantity (about 6·5 per cent.) of material insoluble in chloroform; this has a fibrous structure and swells enormously, but without dissolving, in contact with chloroform, ether, light petroleum, or carbon disulphide, and has the composition $C_{30}H_{64}O_{10}$, which suggests a possible relationship with Spiller's resin, $C_{30}H_{48}O_{10}$, obtained by the oxidation of india-rubber (this Journal, 1865, 3, 44), although the author considers it to be rather a "link between india-rubber and the carbohydrates" than a transformation product of the former. Its composition, however, closely approximates to that of a polyprene hydrate, $C_{30}H_{48} \cdot 10H_2O$. Gladstone and Hibbert's view that it is formed by the action of heat on the india-rubber juice during drying does not appear to be justified; other varieties of india-rubber (Congo-ball, Lagos, Borneo, and Assam) do not contain a portion insoluble in chloroform.

On adding alcohol to the chloroform solution of Para rubber, a precipitate is obtained which, after drying in an atmosphere free from oxygen, has the composition $(C_{10}H_{16})_n$. The same hydrocarbon (polyprene) apparently exists in all varieties of india-rubber, although these contain in addition slightly differing amounts of oxygenated impurities; in all samples, however, the atomic ratio $C:H=10:16$ approximately.

The tetrabromide, $C_{10}H_{16}Br_4$, formed by the action of bromine on polyprene dissolved in chloroform, is obtained as a snow-white mass by pouring the solution into alcohol, and thus prepared, can, after drying, be kept for an indefinite period without decomposing, although Gladstone and Hibbert have stated that it is unstable, rapidly losing hydrogen bromide. It is insoluble in all solvents except chloroform, and even with the latter its solubility varies; it is remarkable that, when recovered chloroform is used in the preparation, the product obtained, although not differing in composition from other samples, is completely insoluble in the solvent named. On the other hand, one preparation was found to be more soluble in benzene than in chloroform. It thus appears that polyprene tetrabromide is capable of undergoing complex physical change. Towards cold fuming nitric acid, and boiling solutions of chromic acid or of chromic and sulphuric acids, on the other hand, the substance is completely indifferent; when heated alone above $50-60^\circ$, hydrogen bromide is evolved, and a dark brown product obtained. On heating with alcoholic sodium ethoxide at 120° , part of the bromine appears to be replaced by ethoxyl.

Contrary to the usual statements, polyprene readily unites with iodine; after 12 hours action at the ordinary temperature in chloroform solution, a *product*, $C_{20}H_{32}I_6$, is obtained, which is insoluble in all solvents except warm aniline or toluidine, and is decomposed on heating at 80° or 100° .

Dry hydrogen chloride below 10° acts indefinitely on polyprene in chloroform solution, but when moist the *dihydrochloride*, $C_{10}H_{18}Cl_2$, is obtained; this is a white, friable mass, which is insoluble in nearly all solvents except chloroform, and on heating at 40° , loses hydrogen chloride until its composition approximates to $C_{10}H_{17}Cl$; on raising the temperature, no further change takes place, so that the mono-

hydrochloride appears to be relatively stable. All attempts to prepare corresponding hydrobromides or hydriodides ended in failure; and the same holds true of all attempts to determine the molecular weight of the substances hitherto described.

On heating polyprene tetrabromide with phenol at 100°, it changes from white to green, then successively through dull grey, dark blue, to purple or crimson, and finally dissolves with evolution of hydrogen bromide; on completing the action by heating for 10 minutes at 150°, a buff-coloured, pulverulent substance having the composition of a *polyprene tetraphenoxide*, $C_{10}H_{16}(OPh)_4$, can be isolated, the yield corresponding with 50 per cent. of the tetrabromide employed; it is readily soluble in aqueous and alcoholic sodium hydroxide, alcohol, acetone, ether, and ethyl acetate, but insoluble in benzene, chloroform, carbon bisulphide, and light petroleum. By limiting the temperature of the action to from 90—95°, and varying the method of isolating the product, substances are obtained which differ in colour from dull crimson to a rich shade of indigo, and correspond in composition with either *dioxypolyprene tetraphenoxide*, $C_{10}H_{16}O_2(OPh)_4$, or with the *compound* $C_{10}H_{16}O_5(OPh)_5$; under one set of conditions, the same product is always obtained. On prolonged boiling with aqueous sodium hydroxide, all these substances lose phenol and yield products containing an increasing number of hydroxyl groups.

A large number of other aromatic hydroxy-compounds behave like phenol with polyprene tetrabromide, but phenol-ethers are without action. W. A. D.

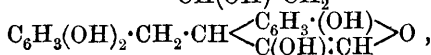
Sugars of some Glucosides. By EMIL VOTOČEK (*Zeit. Zuck.-ind. Böhm.*, 1900, 24, 239—248).—A number of glucosides have been examined to ascertain whether the sugars they yield are hexoses or methylpentoses, the method employed being distillation with 12 per cent. hydrochloric acid. With æsculin, arbutin, apiin, phloridzin, gratiolin, jalapin, ononin, syringin, neither furfuraldehyde nor methylfurfuraldehyde is obtained, showing that their sugars belong to the hexose group. Saponin and cyclamin give small quantities of furfuraldehyde, possibly owing to the presence of impurities, whilst with chinovin, hesperidin, and xanthorhamnin, the amounts of methylfurfuraldehyde obtained prove conclusively the presence of methylpentoses. In the case of convolvulin (rhodeoretin), the methylfurfuraldehyde formed corresponds with an amount of methylpentose equal to 40·6 per cent. of the glucoside, whilst solanin gives 19·6 per cent. of its weight of a methylpentose. T. H. P.

Compounds from Rhubarb and Allied Substances. By CARL LIEBERMANN (*Annalen*, 1900, 310, 364—369. Compare Hesse, this vol., i, 40).—A criticism of the constitutional formulæ employed by Hesse in representing chrysophanic acid, rhabarberone, protophyscion, rhein, and emodin (*loc. cit.*). M. O. F.

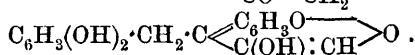
Brazilin. By STANISLAUS VON KOSTANECKI and W. FEUERSTEIN (*Chem. Centr.*, 1900, i, 605—606; from *Arch. Sci. phys. nat. Genève*, [iv], 8, 385—386).—When the diethyl ether of the product obtained

by Schall and Dralle by oxidising brazilin is heated with sodium ethoxide, fisetol diethyl ether, $\text{OH} \cdot \text{C}_6\text{H}_3(\text{OEt}) \cdot \text{CO} \cdot \text{CH}_2 \cdot \text{OEt}$, melting at $42-44^\circ$, and formic acid are formed. The composition of brazilin is

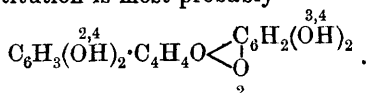
probably $\text{C}_6\text{H}_3(\text{OH})_2 \cdot \text{CH} : \text{C} \begin{smallmatrix} \text{C}_6\text{H}_3(\text{OH}) \\ \text{CH}(\text{OH}) \cdot \text{CH}_2 \end{smallmatrix} \text{O}$ or



and of brazilein, $\text{C}_6\text{H}_3(\text{OH})_2 \cdot \text{CH} : \text{C} \begin{smallmatrix} \text{C}_6\text{H}_3(\text{OH}) \\ \text{CO} - \text{CH}_2 \end{smallmatrix} \text{O}$ or



Since hæmatoxylin does not yield Schall and Dralle's compound on oxidation, its constitution is most probably



E. W. W.

Alkaloids of the Solanaceæ. By JOHANNES GADAMER (*Annalen*, 1900, 310, 352—363. Compare Hesse, this vol., i, 50).—A detailed reply to the criticisms of Hesse respecting the author's investigations of atropine, hyoscyamine, hyoscyne, atropine, and scopolamine.

M. O. F.

Combination of Basic with Acidic Colouring Matters. By ALPHONSE SEYEWETZ (*Compt. rend.*, 1900, 130, 842—844).—It is well known that many basic and acidic colouring matters have the property of combining to form insoluble compounds, but the author finds that similar results are not observed, as a rule, if one of the substances is a non-tinctorial basic or acidic derivative. Acids do not form insoluble compounds with auramine, and bases do not form insoluble compounds with ammonium picrate. Experiments with a large number of substances show that benzene derivatives containing an acidic group or several identical acidic groups such as CO_2H , OH , SO_3H , NO_2 , $\text{CO} \cdot \text{CO}$, &c., do not form precipitates with auramine, but if such compounds contain two or more different groups, they precipitate it. Derivatives containing only one carboxyl and one hydroxyl group are exceptions to this rule, and the introduction of a third group is necessary before insoluble compounds with auramine can be formed. Non-tinctorial amino-derivatives and compounds containing the groups :NH , N: , :N:N: , ON_2 , $\text{:NH} \cdot \text{NH}$, or $\begin{smallmatrix} \text{N} \\ \diagup \quad \diagdown \\ \text{N} \end{smallmatrix}$, or nitrogen in the benzene, naphthalene, or anthracene nuclei do not form precipitates with ammonium picrate. Compounds containing both an amino-group and the diazo-group in the benzene nucleus at first sight seem to be exceptions to this rule, but they are themselves colouring matters. The introduction of a sulphonic group into an aromatic nucleus containing several amino-groups likewise confers on it the property of precipitating auramine.

It follows that the chromophore of the colouring matter plays an

important part in the reaction referred to, and that the formation of the insoluble products in question may be regarded as characteristic of colouring matters.

C. H. B.

Action of Bromoform and Chloroform on some Pyrroles. By O. Bocchi (*Gazzetta*, 1900, 30, i, 89—96).—3-Chloro-2:6-dimethylpyridine, C_7H_8NCl , prepared by the gradual addition of chloroform (1 mol.) to a solution of 2:5-dimethylpyrrole (1 mol.) in an alcoholic solution of sodium ethoxide (2 mols.), is a colourless liquid, heavier than water, in which it is appreciably soluble; its *hydrochloride* crystallises in colourless, deliquescent needles; the *picrate*, $C_{13}H_{11}O_7N_4Cl$, separates from water in aggregates of yellow needles melting at 150 — 151° ; the *aurichloride* crystallises in slender needles melting at 131° , and is soluble in very dilute hydrochloric acid; the *platinichloride* forms orange-yellow needles melting at 212° .

3-Bromo-2:6-dimethylpyridine, C_7H_8NBr , is prepared in like manner to the chloro-compound, and has similar properties. Its *hydrochloride* crystallises in colourless, deliquescent needles, and the *picrate* separates from methyl alcohol in long, yellow needles melting at 148° . On reduction with zinc and dilute hydrochloric acid, the bromo-base yields 2:6-dimethylpyridine.

Bromoform acts on 2:4-dimethylpyrrole in presence of sodium ethoxide, yielding a small quantity of a yellowish oil, which has an intense pyridic odour, and is completely soluble in acids. This oil consists mainly of two pyridine bases, as it gives two distinct *picrates*, which separate from methyl alcohol, the one in long needles melting at 176° , and the other in prisms melting at about 170° . The formation of two different bases is readily explained on theoretical grounds; the compounds were not investigated further, owing to the small yield.

T. H. P.

Action of Amines on Dibromotriacetoneamine. By Hermann Pauly and Carl Boehm (*Ber.*, 1900, 33, 919—923. Compare Pauly and Rossbach, *Abstr.*, 1899, i, 773).—The action of primary and secondary amines on dibromotriacetoneamine is similar to that of ammonia, but no definite substances could be isolated from the product of the action of tertiary or aromatic amines on the base.

By the action of methyl iodide on tetramethylpyrrolinecarboxylmethylamide (Pauly and Rossbach, *loc. cit.*), there is produced the hydriodide of a base which crystallises from light petroleum in long, silky needles, and melts at 108 — 109° ; the same base is also produced in small quantities by the action of methyl iodide on the potassium salt of N-methyltetramethylpyrrolinecarboxylamide, and it must therefore be represented by the formula $NMe \begin{matrix} \diagup CMe_2 \cdot CH \\ \diagdown CMe_2 \cdot C \cdot CO \cdot NHMe \end{matrix}$.

The constitution of tetramethylpyrrolinecarboxylmethylamide has been established by hydrolysing it with fuming hydrochloric acid at 130° , when the hydrochlorides of tetramethylpyrrolinecarboxylic acid and methylamine are obtained.

Tetramethylpyrrolinecarboxylbenzylamide, $C_8H_{14}N \cdot CO \cdot NH \cdot CH_2Ph$, crystallises from water in small, rhombic tablets, and melts at 71° .

Tetramethylpyrrolinecarboxyldimethylamide, $C_8H_{14}N \cdot CO \cdot NMe_2$, boils at 125° under 15 mm. pressure, solidifies at 45° in radiating needles, and is hydrolysed by hydrochloric acid to the hydrochlorides of dimethylamine and the acid. *Tetramethylpyrrolinecarboxylpiperidide*, $C_8H_{14}N \cdot CO \cdot NC_5H_{10}$, boils at 170° under 19 mm. pressure, and solidifies at 74° in radiating needles. T. M. L.

Action of the Sodium Alkylloxides on Ethyl Phthalylaminoacetate and its Homologues. By SIEGMUND GABRIEL and JAMES COLMAN (*Ber.*, 1900, 33, 980—995).—The sodium alkylloxides do not hydrolyse ethyl phthalylaminoacetate, but convert it into derivatives of isoquinoline. Ethyl phthalylaminoacetate is converted by sodium ethoxide into *ethyl 4-hydroxyisocarbostyryl-3-carboxylate*, $C_6H_4 \begin{smallmatrix} \text{CO} \text{---} \text{NH} \\ \text{C(OH):C} \end{smallmatrix} \cdot CO_2Et$, which crystallises in snow-white needles melting at 194° . Sodium methoxide produces a similar change, the corresponding *methyl ester* being formed in silky needles melting at 221 — 222° . The sodium compound, $C_{11}H_8O_4NNa$, is a yellow, crystalline powder.

On treatment with hydrobromic acid, the methyl ester yields *4-hydroxyisocarbostyryl*, $C_6H_4 \begin{smallmatrix} \text{CO} \text{---} \text{NH} \\ \text{C(OH):CH} \end{smallmatrix}$, which crystallises in needles, does not melt below 250° , and readily undergoes oxidation in alkaline solution (compare following abstract); it is converted by reduction with hydriodic acid into *isocarbostyryl*, $C_6H_4 \begin{smallmatrix} \text{CO} \text{---} \text{NH} \\ \text{CH:CH} \end{smallmatrix}$. This substance yields, with phosphorus oxychloride, *1-chloroisoquinoline*, $C_6H_4 \begin{smallmatrix} \text{CCl:N} \\ \text{CH:CH} \end{smallmatrix}$, which melts at 37 — 38° and boils at 274 — 275° . The monochloroisoquinoline previously described must therefore be 3-chloroisoquinoline (Gabriel, *Abstr.*, 1887, 62).

Hydroxyisocarbostyryl is converted by phosphorus oxychloride into two compounds: 1 : 4-*Dichloroisoquinoline*, $C_6H_4 \begin{smallmatrix} \text{CCl:N} \\ \text{CCl:CH} \end{smallmatrix}$, melting at 88 — 89° , is formed in small quantity, whilst the chief product consists of *4-hydroxy-1-chloroisoquinoline*, $C_6H_4 \begin{smallmatrix} \text{CCl=N} \\ \text{C(OH):CH} \end{smallmatrix}$, which crystallises in long, silky needles melting at 195 — 196° . This base is converted by methyl alcoholic potash into *4-methoxy-1-chloroisoquinoline*, $C_6H_4 \begin{smallmatrix} \text{CCl=N} \\ \text{C(OMe):CH} \end{smallmatrix}$, which forms a mass of radiating crystals and melts at 77° . Hydroxychloroisoquinoline is reduced by hydriodic acid and phosphorus to tetrahydroisoquinoline.

Ethyl α -phthalyliminopropionate, $C_8H_8O_2 \cdot N \cdot CHMe \cdot CO_2Et$, is prepared by the action of potassium phthalimide on ethyl α -bromopropionate, and forms colourless crystals melting at 61 — 63° . Sodium methoxide converts it into *4-hydroxy-3-methylisocarbostyryl*,

$C_6H_4 \begin{smallmatrix} \text{CO} \text{---} \text{NH} \\ \text{C(OH):C} \end{smallmatrix} Me + H_2O$, which forms colourless crystals, loses its

water at 200°, and is a weak base, the hydrochloride being decomposed by water. The base is converted by ethyl iodide into 4-methoxy-3-methylisocarbostyryl, which crystallises in needles melting at 195°, and is insoluble in alkalis. Hydriodic acid converts methylhydroxyisocarbostyryl into 3-methylisocarbostyryl, whilst phosphorus oxychloride converts it into 1-chloro-4-hydroxy-3-methylisoquinoline,

$C_6H_4 \begin{smallmatrix} \diagup CCl=N \\ \diagdown C(OH):CMe \end{smallmatrix}$, which is a crystalline powder melting at 163°.

On methylation, this substance yields 1-chloro-3-methyl-4-methoxyisoquinoline, $C_6H_4 \begin{smallmatrix} \diagup CCl=N \\ \diagdown C(OMe):CMe \end{smallmatrix}$, which melts at 49° and boils at 302—304°. Chlorohydroxymethylisoquinoline is converted by reduction

into 3-methyltetrahydroisoquinoline, $C_6H_4 \begin{smallmatrix} CH_2 \cdot NH \\ \diagdown CH_2 \cdot CHMe \end{smallmatrix}$, which boils at 236—237°, and with sodium nitrite yields a nitrosamine, $C_{10}H_{12}N \cdot NO$, crystallising in needles melting at 77—78°. In the preparation of chlorohydroxymethylisoquinoline, 1:4-dichloro-3-

methylisoquinoline, $C_6H_4 \begin{smallmatrix} \diagup CCl:N \\ \diagdown CCl:CMe \end{smallmatrix}$, is obtained in small quantity as a hard, crystalline mass, which melts at 95°, boils at 300—312°, yields 3-methylisoquinoline on reduction with hydriodic acid, and is converted by sodium methoxide into 4-chloro-1-methoxy-3-methylisoquinoline, $C_6H_4 \begin{smallmatrix} \diagup C(OMe):N \\ \diagdown CCl=CMe \end{smallmatrix}$, which crystallises in slender needles melting at 57—58°.

Ethyl α -phthalyliminobutyrate, $C_8H_4O_2N \cdot CHEt \cdot CO_2Et$, boils at 333—337°, and is converted by sodium methoxide into 4-hydroxy-3-ethylisocarbostyryl, $C_6H_4 \begin{smallmatrix} \diagup CO-NH \\ \diagdown C(OH):CEt \end{smallmatrix}$, which crystallises in lustrous needles. The hydrochloride, $C_{11}H_{11}O_2N \cdot HCl$, is decomposed by water; hydriodic acid reduces it to 3-ethylisocarbostyryl.

Benzylphthalimide does not react in a similar manner to the phthalylaminoacetic ester, but is converted by sodium methoxide into benzylphthalamic acid.

A. H.

4-Hydroxyisocarbostyryl. By SIEGMUND GABRIEL and JAMES COLMAN (*Ber.*, 1900, 33, 996—1000. Compare the foregoing abstract).

—4-Hydroxyisocarbostyryl, $C_6H_4 \begin{smallmatrix} \diagup C(OH) \\ \diagdown CO \cdot NH \end{smallmatrix} > CH$, resembles indoxyl in constitution, and, like the latter, readily undergoes oxidation, the product, $C_6H_4 \begin{smallmatrix} \diagup CO \\ \diagdown CO \cdot NH \end{smallmatrix} > C:C \begin{smallmatrix} \diagdown CO \\ \diagup NH \cdot CO \end{smallmatrix} > C_6H_4$, termed by the author *carbindigo*, bearing to indigo the same relation as the original compound bears to indoxyl.

Carbindigo is formed from hydroxyisocarbostyryl by the action of ferric chloride on its acid solution, or by the spontaneous oxidation of its alkaline solution in the air. It is insoluble in the usual solvents, but crystallises from nitrobenzene in flat, ruby-red needles, which melt above 400°. It is converted by alkalis into a brown mass and dissolves in warm aqueous potash. It is reduced by alcoholic

ammonium sulphide to a yellow "leuco-compound," $C_{18}H_{12}O_4N_2$, which is an insoluble, lemon-yellow, crystalline powder. On oxidation with fuming nitric acid, carbindigo yields *phthalonimide*, $C_6H_4 \begin{smallmatrix} \text{CO} \cdot \text{NH} \\ \diagup \quad \diagdown \\ \text{CO} \cdot \text{CO} \end{smallmatrix}$, which melts and decomposes at $198-220^\circ$; the formation of this substance is quite analogous to that of isatin from indigo. On hydrolysis, phthalonimide yields phthalonic acid and *phthalonamic acid*, $NH_2 \cdot CO \cdot C_6H_4 \cdot CO \cdot CO_2H$, which crystallises, with $1\frac{1}{2}H_2O$, in short, compact prisms and melts and decomposes at $178-179^\circ$. The *silver salt* crystallises in flat needles. Phthalonamic acid is converted by alkali hypochlorite into isatic acid, its constitution being thus established. A. H.

Synthesis of Indoline Bases. By KARL BRUNNER (*Monatsh.*, 1900, 21, 156—183. Compare Abstr., 1898, i, 384 and 682).—The bases obtained by E. Fischer (*loc. cit.*) and analogous compounds are best represented by formulæ of the type, $C_6H_4 \begin{smallmatrix} \text{CMe}_2 \\ \diagup \quad \diagdown \\ \text{NPh} \end{smallmatrix} > C:CH_2$, and the corresponding salts by $C_6H_4 \begin{smallmatrix} \text{CMe}_2 \\ \diagup \quad \diagdown \\ \text{NCIPh} \end{smallmatrix} > CMe$.

1-Phenyl-3:3-dimethyl-2-methyleneindoline forms a *stannochloride*, $C_{17}H_{17}N \cdot HSnCl_3$, which crystallises in lustrous, yellow tablets melting at $121-122^\circ$; a *mercurichloride*, which melts at 189° to a violet mass; a *ferrichloride*, which forms small, yellow needles melting at 162° , and a *platinichloride* which melts at 198° .

1-Phenyl-3:3-dimethyl-2-indolinol is prepared by decomposing with potassium hydroxide the indefinite *tin salt* obtained by treating *isobutylidenediphenylhydrazine* with an alcoholic solution of stannous chloride; it crystallises from benzene with $\frac{1}{4}C_6H_6$ in lustrous, colourless prisms, which melt between 110° and 115° , lose the benzene of crystallisation on keeping, and then melt at 125° ; it forms a *mercurichloride*, $C_{16}H_{15}N \cdot HHgCl_3$, which melts and decomposes at 124° ; its solution in hydrochloric acid is a delicate reagent for nitrites, which produce a violet-blue coloration; oxidation in alkaline solution converts it into 1-phenyl-3:3-dimethyl-2-indolinone, which forms colourless crystals melting at 72° and boiling at $210-212^\circ$ under 30 mm. pressure. On boiling a solution of 1-phenyl-3:3-dimethyl-2-indolinol with hydrochloric acid, it is converted into 1-phenyl-2:3-dimethylindole, which is a viscous, fluorescent oil boiling at $228-230^\circ$ under 60 mm. pressure; this forms a *picrate* melting at 131° , and with methyl iodide yields the hydriodide of 1-phenyl-3:3-dimethyl-2-methyleneindoline.

R. H. P.

Syntheses in the Acridine Series. I. 2'-Methyl-1:2-naphth-acridine.* By FRITZ ULLMANN and E. NAEF (*Ber.*, 1900, 33, 905—912).—When dihydroxydinaphthylmethane, $CH_2(C_{10}H_6 \cdot OH)_2$, the condensation product of formaldehyde with β -naphthol (Abel, Abstr., 1893, i, 172; Manasse, 1894, i, 577) is heated with a mixture of *p*-toluidine and its hydrochloride, eventually to 200° , β -naphthol is obtained along with a dihydroacridine and an acridine, the last result-

* The names assigned to the compounds described in these papers are misleading, as methylnaphthacridine would have the formula $C_{22}H_{15}N$, not $C_{18}H_{13}N$.

ing from a partial oxidation of the leuco-compound by the oxygen of the air. The same result is obtained when either of the condensation products of formaldehyde with *p*-toluidine, methylenedi-*p*-tolylidimide (Eberhardt and Welter, Abstr., 1894, i, 451) or anhydroformaldehyde-*p*-toluidine, is heated with β -naphthol; and also when β -naphthol, *p*-toluidine and trioxymethylene (paraformaldehyde) are heated together.

"Methylnaphthacridine," $C_6H_4 \begin{array}{c} \diagup C \cdot CH \cdot C \cdot CH \cdot CMe \\ \diagdown CH \cdot CH \cdot C \cdot N \cdot C \cdot CH \cdot CH \end{array}$, melts at 158° and boils at 460° ; it is almost white, but the salts are yellow. These are comparatively little soluble in water; the *hydrochloride*, *nitrate*, and *picrate* were prepared (the base is a monoacid one); with 4 per cent. fuming sulphuric acid, it yields a pale yellow *monosulphonic acid*. "Methyldihydronaphthacridine," $C_{18}H_{15}N$, is colourless and melts at $190-193.5^\circ$. C. F. B.

Syntheses in the Acridine Series. II. 2'-Methyl-3'-amino-1:2-naphthacridine. By FRITZ ULLMANN and E. NAEF (*Ber.*, 1900, 33, 912-919).—When *m*-tolylenediamine is treated with formaldehyde in neutral (aqueous or alcoholic) solution at the ordinary temperature, the product is anhydroformaldehyde-*m*-tolylenediamine, $C_8H_{10}N_2$, which melts between 150° and 180° ; formaldehyde can be obtained from it and detected by Tollens' method (this vol., i, 56), and so Schiff's view of its constitution (Abstr., 1891, 1258) is correct, not so that of Terisse (*Chem. Zeit.*, 1899, 286). In dilute sulphuric acid solution at 60° , the product is tetraminoditolylmethane, $CH_2[C_6H_2Me(NH_2)_2]_2$, which melts at $203-204^\circ$.

When a mixture of *m*-tolylenediamine and its hydrochloride is heated with dihydroxydinaphthylmethane, when β -naphthol is heated with anhydroformaldehyde-*m*-tolylenediamine, or with tetraminoditolylmethane, and when *m*-tolylenediamine, β -naphthol and trioxymethylene are heated together, "aminomethylnaphthacridine" and its dihydro-(leuco) compound are formed in all cases (compare preceding abstract). "Aminomethylnaphthacridine," $C_{10}H_6 \begin{array}{c} CH \\ | \\ N \end{array} C_6H_2Me \cdot NH_2$, melts at 244° (corr.), is yellow, is a monoacid base, and forms coloured salts; of these, the *hydrochloride* and *platinichloride* were prepared. The *monoacetyl* derivative melts at $320-321^\circ$ (corr.), is almost colourless, and is readily hydrolysed by boiling dilute hydrochloric acid. "Aminomethyldihydronaphthacridine," $C_{18}H_{16}N_2$, is almost colourless and melts at $195-198^\circ$. C. F. B.

Compounds of Iodoantipyrine with Mercuric Salts. By J. BOUGAULT (*J. Pharm.*, 1900, [vi], 11, 165-169).—*Iodoantipyrine mercuric chloride*, $C_{11}H_{11}ON_2I \cdot HgCl_2$, forms beautiful, colourless crystals, melts and decomposes at $168-169^\circ$, and is stable in aqueous solution. Mercuric iodide does not combine directly with iodoantipyrine, but on adding iodine to an alcoholic solution of antipyrine containing mercuric iodide, the salt, $2C_{11}H_{11}ON_2I \cdot HgI_2$, separates in bright yellow crystals. The compound, $4C_{11}H_{11}ON_2I \cdot HgCl_2 \cdot HgI_2 \cdot 2HCl$, prepared by mixing alcoholic solutions of the component salts, forms slightly yellow crystals, melts and decomposes at about 140° , and is rapidly

dissociated by water. The salt $2C_{11}H_{11}ON_2I \cdot HgI_2 \cdot HCl$ (this vol., i, 312) forms bright yellow crystals and melts and decomposes at 130° .

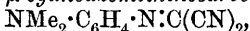
W. A. D.

New Compound of Mercuric Chloride and Antipyrine. By JULES VILLE and CHARLES ASTRE (*Compt. rend.*, 1900, 130, 837—840).—When a solution of mercuric chloride, containing also sodium chloride and hydrochloric acid, is added slowly to an aqueous solution of antipyrine, the compound $(C_{11}H_{12}ON_2)_2 \cdot HHgCl_3$, is obtained in rhomboidal lamellæ which melt at 105 — 106° , and dissolve readily in chloroform. Its solutions give many of the ordinary reactions of mercuric compounds, but with sodium carbonate and sodium hydrogen carbonate there is no precipitate or turbidity, whilst potassium iodide yields a very slightly yellowish precipitate soluble in excess of the reagent to a yellowish solution. In the latter reactions, and also in its behaviour with stannous chloride and auric chloride, this compound differs from that described by Hirsch and by Schuyten (*Abstr.*, 1896, i, 575; and 1898, i, 452). It gives, however, the ordinary reactions of antipyrine.

C. H. B.

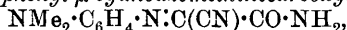
Condensation of Aromatic Nitroso-compounds with Methylene Derivatives. By FRANZ SACHS (*Ber.*, 1900, 33, 959—966. Compare *Abstr.*, 1899, i, 883).—4-Diethylaminophenyl- μ -cyanoazomethine-phenyl yields a crystalline *hydrochloride* when hydrogen chloride is passed into its benzene solution; in the perfectly dry state, this may be kept for months without undergoing decomposition; its chloroform solution is, however, decomposed when poured on to a dry filter paper. When the dye is heated with alcohol and hydroxylamine hydrochloride, it yields the oxime of benzoyl cyanide (*Abstr.*, 1888, 693). The *hydrochloride* of 4-diethylaminophenyl- μ -cyanoazomethine-4'-nitrophenyl is a lemon-yellow powder melting and decomposing at 193° .

4-Dimethylaminophenyl- μ -cyanoazomethinecarboxylonitrile,



is readily obtained when nitrosodimethylaniline and malonitrile are heated together in alcoholic solution, either with or without the addition of a few drops of sodium carbonate solution; it crystallises from alcohol in dark red crystals with a bronzy lustre, melts at 167° , and is insoluble in light petroleum; sulphuric acid hydrolyses it to dimethylphenylenediamine, carbon dioxide and hydrogen cyanide. The *diethyl* compound, $NEt_2 \cdot C_6H_4 \cdot N : C(CN)_2$, crystallises in brownish-violet needles or violet-red, glistening plates melting at 114° .

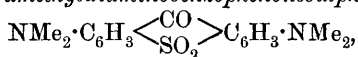
4-Dimethylaminophenyl- μ -cyanoazomethinecarboxylamide,



obtained from nitrosodimethylaniline and cyanoacetamide in the presence of alcohol and sodium carbonate solution, crystallises in rose-coloured, slender needles with a blue lustre, and melts at 220 — 221° , the *diethyl* compound melts at 165 — 166° , and is sparingly soluble in cold alcohol. A compound, $SO_2 \langle C_6H_3(NMe_2) \rangle C : N \cdot C_6H_4 \cdot NMe_2$,

is obtained when an alcoholic solution of nitrosodimethylaniline and and tetramethyldiaminodiphenylmethanesulphone is warmed with a little sodium hydroxide solution; it is an orange-red powder, and is

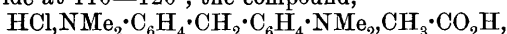
very sparingly soluble in the usual solvents. If the crude product is boiled, it yields *tetramethyldiaminobenzophenonesulphone*,



in the form of a yellowish-green precipitate which melts at 317° (corr.), sublimes at higher temperatures, and is extremely stable.

J. J. S.

Action of Methyl Chloroacetate on Tertiary Bases. By J. CENSI (*Chem. Centr.*, 1900, i, 594—595; from *Bull. Soc. ind. Mulhouse*, 70, 311—313).—Methyl chloroacetate, $\text{CH}_2\text{Cl} \cdot \text{CO}_2\text{Me}$, prepared by the action of chlorine on cold methyl acetate, boils at 115° . By condensing this compound (1 mol.) with dimethylaniline (2 mols.) in the presence of zinc chloride at 110 — 120° , the compound,



is obtained. When methyl chloroacetate is poured into boiling water hydrochloric acid, acetic acid, and formaldehyde are formed.

E. W. W.

Interaction of Hydrazine Hydrate with certain Lactones. By JEAN WEDEL (*Ber.*, 1900, 33, 766—770).—*o*-Hydroxydiphenylacetic hydrazide, $\text{OH} \cdot \text{C}_6\text{H}_4 \cdot \text{CHPh} \cdot \text{CO} \cdot \text{NH} \cdot \text{NH}_2$, prepared by boiling *o*-hydroxydiphenylacetic lactone (*Abstr.*, 1895, i, 419) dissolved in absolute alcohol with aqueous hydrazine hydrate, crystallises from absolute alcohol in microscopic, colourless, lustrous needles, and melts and decomposes at 220° ; it gives Bülow's reaction for phenylhydrazides, and dissolves in aqueous alkalis, being recovered unchanged by the action of carbon dioxide; this behaviour excludes the alternative formula, $\begin{array}{c} \text{CHPh} \\ | \\ \text{C}_6\text{H}_4 \cdot \text{O} \end{array} \text{C}(\text{OH}) \cdot \text{NH} \cdot \text{NH}_2$, for the substance. It unites at

the ordinary temperature with benzaldehyde, yielding the *benzylidene* derivative, $\text{OH} \cdot \text{C}_6\text{H}_4 \cdot \text{CHPh} \cdot \text{CO} \cdot \text{NH} \cdot \text{N} \cdot \text{CHPh}$, which crystallises from alcohol in plates, and melts at 171° ; *o*-phthalaldehydic acid gives rise to the corresponding compound,



which dissolves in cold aqueous sodium carbonate, crystallises from alcohol in colourless plates, and decomposes at 145° .

o-Methylolbenzoic hydrazide, $\text{OH} \cdot \text{CH}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{CO} \cdot \text{NH} \cdot \text{NH}_2$, prepared by gently warming aqueous hydrazine hydrate with an alcoholic solution of phthalide, crystallises from alcohol in long, slender needles, melts at 128° , and does not give Bülow's reaction; all attempts to

convert it into the dihydrophthalazone, $\text{C}_6\text{H}_4 \begin{array}{c} \text{CH}_2 \cdot \text{NH} \\ \text{CO} - \text{NH} \end{array}$, by eliminating water by means of concentrated sulphuric acid, phosphorus pentachloride, or phosphorus oxychloride, yielded phthalide only. Attempts to prepare the same compound by the interaction of hydrazine hydrate with phthalide chloride, $\text{CH}_2\text{Cl} \cdot \text{C}_6\text{H}_4 \cdot \text{COCl}$, were also fruitless. The *benzylidene* derivative, $\text{C}_{15}\text{H}_{14}\text{O}_2\text{N}_2$, obtained by the interaction of benzaldehyde with *o*-methylolbenzoic hydrazide, crystallises from alcohol in lustrous leaflets, and melts at 145° ; its *carboxylic acid*,

$C_{16}H_{14}O_4N_2$, prepared similarly, using *o*-phthalaldehydic acid, forms needles, and melts at 115° .

No definite products could be isolated from the interaction of hydrazine hydrate with valerolactone or coumarin. Nitrous acid does not act on the hydrazides described, whilst acetic anhydride, instead of yielding acetyl derivatives, regenerates the original lactones.

W. A. D.

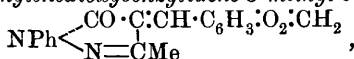
Indogenides of the Pyrazole Series. By JOSEF TAMBOR (*Ber.*, 1900, 33, 864—871. Compare Knorr, *Abstr.*, 1887, 601).—[With ERNST.]—1-Phenyl-4-*o*-ethoxybenzylidene-3-methyl-5-pyrazolone,

$$NPh \begin{array}{l} \diagup CO \cdot \dot{C} : CH \cdot C_6H_4 \cdot OEt \\ \diagdown N = CMe \end{array}$$
, prepared by heating 'technical pyrazolone' (1-phenyl-3-methyl-5-pyrazolone) with *o*-ethoxybenzaldehyde at 135° during 5—10 minutes, crystallises from alcohol in orange needles, and melts at 142° ; the solution in concentrated sulphuric acid is carmine. The corresponding *m*-ethoxy-compound crystallises in orange prisms, and melts at 107° ; the solution in sulphuric acid is brown, becoming yellow on dilution with water. The *p*-ethoxy-compound separates from dilute acetic acid in orange needles, and melts at 130° . The *p*-methoxy-compound, prepared from pyrazolone and anisaldehyde, crystallises from alcohol, and melts at 128.5° ; the solution in concentrated sulphuric acid is yellow. The *p*-hydroxy-compound crystallises in orange needles and melts at 226° , forming a greenish-yellow solution in concentrated sulphuric acid; the *acetyl* derivative melts at 137° .

[With LICIŃSKI.]—1-Phenyl-4-*p*-hydroxy-*m*-methoxybenzylidene-3-methyl-5-pyrazolone,
$$NPh \begin{array}{l} \diagup CO \cdot \dot{C} : CH \cdot C_6H_3(OMe) \cdot OH \\ \diagdown N = CMe \end{array}$$
, prepared from pyrazolone and vanillin, crystallises from ether in lustrous, red prisms, and melts at 169° ; the *acetyl* derivative melts at 143 — 144° . The *mp*-dimethoxy-compound forms long, lustrous needles, and melts at 160° , dissolving in sulphuric acid to an orange liquid.

4-*p*-Hydroxy-*m*-methoxybenzylidene-bis-1-phenyl-3-methyl-5-pyrazolone, $OH \cdot C_6H_3(OMe) \cdot CH(C_{10}H_9ON_2)_2$, produced on heating vanillin with 2 mols. of pyrazolone at 160° for 10 minutes, crystallises from alcohol in yellow needles, and melts at 209° ; the solution in concentrated sulphuric acid is orange.

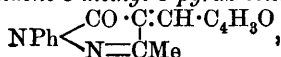
1-Phenyl-*mp*-methylenedioxybenzylidene-3-methyl-5-pyrazolone,



prepared from pyrazolone and piperonaldehyde, crystallises from alcohol in deep red, lustrous needles, and melts at 166 — 167° .

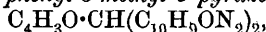
4-*mp*-Methylenedioxybenzylidene-bis-1-phenyl-3-methyl-5-pyrazolone, $CH_2 : O_2 : C_6H_3 \cdot CH(C_{10}H_9ON_2)_2$, obtained on heating piperonaldehyde with 2 mols. of pyrazolone, crystallises in small, white needles, which melt and evolve gas at 143° ; the solution in concentrated sulphuric acid is reddish-yellow.

1-Phenyl-4-furfurylidene-3-methyl-5-pyrazolone,



prepared from furfuraldehyde and pyrazolone, crystallises from alcohol in violet needles, and melts at 111—112°; the solution in concentrated sulphuric acid is brownish-black.

4-Furfurylidene-bis-1-phenyl-3-methyl-5-pyrazolone,

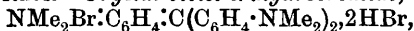


produced on heating furfuraldehyde with 2 mols. of pyrazolone, crystallises from alcohol in pale brown prisms, and melts at 172—173°; when treated with concentrated sulphuric acid, the crystals become blue, a green solution being formed.

M. O. F.

Tertiary Aromatic Amines. III. By CARL HAEUSSERMANN (*Ber.*, 1900, 33, 939—941. Compare Abstr., 1899, i, 204 and 684).—*Nitrotetraphenyl-o-phenylenediamine*, $\text{C}_{30}\text{H}_{23}\text{O}_2\text{N}_3$, prepared by the action of nitrous acid on tetraphenyl-*o*-phenylenediamine, crystallises from glacial acetic acid in brownish-yellow needles and melts at 186—187°. *m*-Dichlorobenzene, when treated with potassium diphenylamine, gives the same condensation product as *o*-dichlorobenzene, owing to isomeric change, and the nitro-derivatives are also identical; β -tetraphenylphenylenediamine, however, appears to be an entirely different compound, in spite of the proximity of the melting points. T. M. L.

Salts and Bases of Triphenylmethane Dyes. By ARTHUR HANTZSCH (*Ber.*, 1900, 33, 752—760. Compare Hantzsch and Osswald, this vol., i, 256).—By leading dry hydrogen bromide into a solution of the leuco-base in ether-acetone at -15° , *crystal-violet-leucohydroxide trihydrobromide*, $\text{OH}\cdot\text{C}(\text{C}_6\text{H}_4\cdot\text{NMe}_2)_3\cdot 3\text{HBr}$, separates as a white, flocculent precipitate. *Crystal-violet trihydrobromide*,



is precipitated as a reddish powder on passing hydrogen bromide into a warm solution of the colour base; it dissolves in water with a deep violet colour even at 0° , owing to decomposition into the monoacid salt and hydrogen bromide.

The salts of the colour-base have a much higher conductivity than the carbinol salt; thus crystal-violet trihydrochloride gave μ_{256} 774 at 25° , and crystal-violet carbinol trihydrobromide gave μ_{256} 471; the carbinol trihydrobromide gradually passes in solution into the trihydrobromide of the colour-base, the conductivity increasing in one experiment from μ_{261} 452 to 792. The carbinol trihydrobromide resembles the aniline salts in that it is partially hydrolysed in solution, but the colour-trihydrobromide decomposes in solution into 2 mols. of hydrogen bromide, and the monohydrobromide, which is ionised, but not hydrolysed, since the colour-base is comparable with potassium hydroxide rather than with aniline.

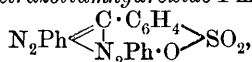
On adding sodium hydroxide to a dilute solution of magenta, or 'new-magenta,' the ammonium colour-base is first formed (rosanilinium hydroxide), but with an excess of alkali a red, flocculent precipitate separates which dissolves readily in ether, benzene, or acetone to a reddish-yellow solution, and is readily precipitated by carbon dioxide as a dark red carbonate (Homolka, Nietzki's "Chemie der organischen Farbstoffe," p. 119); this is regarded as an imide-base, $\text{NH}\cdot\text{C}_6\text{H}_4\cdot\text{C}(\text{C}_6\text{H}_4\cdot\text{NH}_2)_2$, the anhydride of the rosanilinium hydroxide, $\text{OH}\cdot\text{NH}_2\cdot\text{C}_6\text{H}_4\cdot\text{C}(\text{C}_6\text{H}_4\cdot\text{NH}_2)_2$, into which it rapidly passes in solution, or in the solid state, or

when dried, or when left in contact with the solution from which it is precipitated; when changed in this way, the colour disappears and the base is no longer precipitated by carbon dioxide. The imide-base could not be analysed, but no such bases are formed from the completely alkylated colour-salts, thus confirming the view that they are formed by loss of 1 mol. of water; this view is also confirmed by their solubility in ether, since the mixture of 1 mol. magenta and 1 mol. sodium hydroxide cannot be extracted with ether. T. M. L.

Colouring Matters of the Formazyl Group. By FRITZ FICHTER and EMANUEL SCHIESS (*Ber.*, 1900, 33, 747—752).—*Sodium formazylbenzene-II-p-sulphonate*, $\text{N}_2\text{Ph}\cdot\text{CPh}\cdot\text{N}\cdot\text{NH}\cdot\text{C}_6\text{H}_4\cdot\text{SO}_3\text{Na}$, prepared by the action of diazobenzene on sodium phenylbenzylidenehydrazone-*p*-sulphonate, crystallises from alcohol in minute, dark red needles, decomposes at about 135° , and dyes silk and wool a dark red colour; when warmed with sulphuric and acetic acids, it gives 3-phenylphenotriazine, $\text{C}_6\text{H}_4\cdot\begin{smallmatrix} \text{N}:\text{N} \\ \diagup \quad \diagdown \\ \text{N}:\text{CPh} \end{smallmatrix}$, and aniline, but no sulphanilic acid; with zinc dust and sulphuric acid, it gives phenylhydrazine and *s*-benzoylphenylhydrazine-*p*-sulphonic acid, $\text{COPh}\cdot\text{NH}\cdot\text{NH}\cdot\text{C}_6\text{H}_4\cdot\text{SO}_3\text{H}$, which crystallises from water in thin, colourless flakes.

Sodium formazylbenzene-III-p-sulphonate, $\text{NHPh}\cdot\text{N}:\text{CPh}\cdot\text{N}_2\cdot\text{C}_6\text{H}_4\cdot\text{SO}_3\text{Na}$, prepared by the action of diazobenzene-*p*-sulphonic acid on phenylbenzylidenehydrazone, crystallises from alcohol in minute, red needles, decomposes at about 165° , and dyes a somewhat brighter colour than the preceding isomeride; like its isomeride, it gives with sulphuric acid phenylphenotriazine in place of the expected sulphonic acid, and with zinc dust and sulphuric acid gives *s*-benzoylphenylhydrazine-*p*-sulphonic acid.

Sodium formazylbenzene-I-m-sulphonate, $\text{N}_2\text{Ph}\cdot\text{C}(\text{C}_6\text{H}_4\cdot\text{SO}_3\text{Na})\cdot\text{N}\cdot\text{NHPh}$, prepared by the action of diazobenzene on the condensation product of sodium benzaldehyde-*m*-sulphonate and phenylhydrazine, crystallises from alcohol in red needles, and is much more soluble than the preceding isomerides. On oxidation with nitrous acid, it gives the inner anhydride of triphenyltetrazoliumhydroxide-I-m-sulphonic acid,



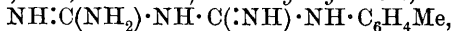
which crystallises from dilute hydrochloric acid in small, four-sided tablets, does not melt at 250° , and is not attacked by acids, but is decomposed by alkalis with formation of a red coloration. The isomerides are still less soluble and are less well characterised.

II-Phenyl-III- α -naphthylformazylbenzene, $\text{NHPh}\cdot\text{N}:\text{CPh}\cdot\text{N}_2\cdot\text{C}_{10}\text{H}_7$, crystallises from benzene in dark violet needles with a green metallic lustre, and melts at 173° ; with sulphuric acid, it gives aniline and phenylnaphthotriazine, $\text{C}_{10}\text{H}_6\cdot\begin{smallmatrix} \text{N}:\text{N} \\ \diagup \quad \diagdown \\ \text{N}:\text{CPh} \end{smallmatrix}$, which crystallises from alcohol in yellowish-green needles and melts at 145° .

III-Phenyl-II- α -naphthylformazylbenzene, $\text{C}_{10}\text{H}_7\cdot\text{NH}\cdot\text{N}:\text{CPh}\cdot\text{N}_2\text{Ph}$,

crystallises from benzene or from a mixture of alcohol and chloroform in deep violet needles and melts at 144—145°; it gives the same triazine as the preceding isomeride. T. M. L.

Tolyldiguanides and Benzyldiguanide. By ERNST BEUTEL (*Annalen*, 1900, 310, 335—351).—*o*-Tolyldiguanide,



crystallises from water in nacreous plates containing $\frac{1}{2}\text{H}_2\text{O}$, and melts at 144°; boiling alkalis liberate *o*-toluidine, and the aqueous solution yields precipitates with salts of copper, nickel, cobalt, or silver. The *hydrochloride*, prepared by heating *o*-toluidine hydrochloride with dicyanodiamide in molecular proportion, crystallises from water in large, colourless prisms containing $\frac{1}{2}\text{H}_2\text{O}$, which is removed by exposure to dried air; the anhydrous substance melts at 229°. The *platinichloride* crystallises from dilute hydrochloric acid in orange-red, rhombic plates, and melts at 199°.

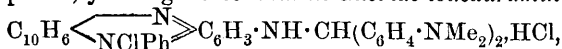
m-Tolyldiguanide, $\text{C}_9\text{H}_{13}\text{N}_5$, crystallises in nacreous scales containing $3\text{H}_2\text{O}$, and melts at 76°; the *hydrochloride*, which contains $\frac{1}{2}\text{H}_2\text{O}$, crystallises in the monosymmetric system, and melts at 211°.

p-Tolyldiguanide, $\text{C}_9\text{H}_{13}\text{N}_5$, crystallises in colourless leaflets and melts at 152°; the *hydrochloride* contains $\frac{1}{2}\text{H}_2\text{O}$ and melts at 235°; the *sulphate* is anhydrous, and the *chromate*, which contains $2\frac{1}{2}\text{H}_2\text{O}$, decomposes at 166°.

Benzyldiguanide, $\text{NH}:\text{C}(\text{NH}_2)\cdot\text{NH}\cdot\text{C}(\text{:NH})\cdot\text{NH}\cdot\text{CH}_2\text{Ph}$, absorbs carbon dioxide so readily that an examination of the substance is a matter of some difficulty; the *hydrochloride*, prepared by heating benzylamine hydrochloride with dicyanodiamide, crystallises in colourless, lustrous plates, and melts at 197°, decomposing above 260°.

A summary of the general properties of these substances and their solubility relationships concludes the paper. M. O. F.

Action of Tetramethyldiaminobenzhydrol on Rosinduline and on Isorosinduline. By RICHARD MÜHLAU and W. SCHAPOSCHNIKOFF (*Ber.*, 1900, 33, 799—803).—Rosinduline chloride does not react with tetramethyldiaminobenzhydrol, whereas Nietzki-Otto's isorosinduline chloride readily reacts with an alcoholic solution of the same compound, yielding *isorosinduline chloride-leucauramine*,



which crystallises with $5\text{H}_2\text{O}$. It dissolves readily in alcohol, and moderately in water, to reddish-violet solutions which do not exhibit fluorescence; acid liquids readily hydrolyse it, even in the cold, as also do neutral salts such as sodium chloride or nitrate. The *base* crystallises from benzene or ether in violet, acicular prisms. The *chromate*, *picrate*, *tannate*, and double salts with zinc, mercury, gold, or platinum are all insoluble in water. The *platinichloride*, $\text{C}_{39}\text{H}_{37}\text{N}_5\text{PtCl}_6$, forms a reddish-violet, crystalline precipitate. J. J. S.

Dynamical Researches on the Formation of Azo-Dyes. IV. By HEINRICH GOLDSCHMIDT and GUSTAV KEPPELER (*Ber.*, 1900, 33, 893—905. Compare *Abstr.*, 1897, i, 278; 1898, ii, 20; 1899, ii, 276).—The reaction of sodium benzenediazotate with sodium β -naphthoxide

and *m*-tolylxide has been investigated, and the results are found to confirm the conclusion arrived at already, namely, that the actual "coupling" takes place between the diazobenzene hydroxide and the phenol, which exist in the solution owing to the hydrolysis of the respective salts. Further experiments with sodium *syn*-diazobenzene-sulphonate and *m*-tolylxide confirm the previous results, and show that the presence of a considerable quantity of potassium chloride has little influence on the velocity of the reaction. Experiments with thymol and sodium benzenediazotate or *syn*-diazobenzenesulphonate did not give satisfactory results.

Experiments were also made with an *isodiazo*-compound: sodium *p*-nitrobenzeneisodiazotate ("nitrosamine-red") was allowed to react with sodium β -naphthoxide at 20; in the estimation of the unchanged *isodiazo*-compound, it was found necessary to add cuprous chloride solution, as mere boiling with dilute acid did not suffice to expel all the nitrogen. In this case, as in the others, it was found that the times in which equal fractions are transformed are proportional to the concentrations, and that excess of alkali hydroxide retards the reaction. Curiously enough, however, the numerical results are rather in harmony with the supposition that of one of the substances it is the hydrolysed part that reacts, whilst the other substance reacts as if its concentration were constant.

C. F. B.

Abel's Dibenzenearazo- β -dinaphtholmethane and Dinitroso- β -dinaphtholmethane. By RICHARD MOHLAU and ERICH STROHBACH (*Ber.*, 1900, 33, 804—807).—These two compounds described by Abel (*Abstr.*, 1893, i, 172) are shown to be respectively benzenearazo- β -naphthol and α -nitroso- β -naphthol. Slight modifications in the preparation of β -dinaphtholmethane are recommended.

J. J. S.

Phenylcarbamic Ester of Epinephrine. By JOHN J. ABEL (*Proc. Amer. Physiol. Soc.*, Dec., 1899; *Amer. J. Physiol.*, 1900, 3, xvii—xviii).—The formation of a substance which is shown to be the sulphate of epinephrine phenylcarbamate, $C_{17}H_{13}O_2N(CO_2 \cdot NHPh)_2 \cdot H_2SO_4$, is believed to demonstrate that epinephrine is a chemical individual. Although two of the hydroxyl groups have entered into combination with phenylcarbamide, physiological activity is retained.

W. D. H.

Action of Triethylphosphine on $\omega\omega$ -Dibromo-*o*-xylene. By ALFRED PARTHEIL and A. GRONOVER (*Ber.*, 1900, 33, 606—607).— $\omega\omega$ -Dibromo-*o*-xylene reacts with triethylphosphine dissolved in chloroform to form *o*-xyleneditriethylphosphonium bromide, $C_6H_4(CH_2 \cdot PET_3Br)_2$, a neutral substance forming colourless crystals which melt at 250—250.5°. The corresponding base is strongly alkaline and very unstable; the *hydriodide*, $C_6H_4(CH_2 \cdot PET_3I)_2 \cdot 2HI$, melts at 247°. The *aurichloride*, $C_6H_4(CH_2 \cdot PET_3 \cdot AuCl_4)_2$, crystallises in yellow needles melting at 163°, and the *platinichloride*, $C_6H_4(CH_2 \cdot PET_3)_2PtCl_6$, is an amorphous powder which melts at 235—236°.

R. H. P.

Organic Chemistry.

Relation Between Boiling Point and Melting Point in the Hydrocarbons. By THOMAS BAYLEY (*Chem. News*, 1900, 81, 1—3).—The ratio (boiling point under 760 mm. pressure)/(melting point) in the paraffin series varies from 1.25 for CH_4 to 2.0 for $\text{C}_{19}\text{H}_{40}$. Above C_{19} , the boiling point is taken at 15 mm. pressure and the ratio varies between 1.53 and 1.73 for the higher members of the series; altogether, the boiling point rises relatively more than the melting point. The values of the ratio are deduced for the ethylene and acetylene series as well as for a number of closed chain hydrocarbons, but no general law is laid down which governs these values. J. C. P.

Action of Anhydrous Aluminium Chloride on Acetylene. By E. BAUD (*Compt. rend.*, 1900, 130, 1319—1322. Compare Alexander, Abstr., 1899, i, 843).—Dry acetylene is completely absorbed by anhydrous aluminium chloride even in the cold, and at 70° the absorption is complete in a few minutes. When the gas is passed over the chloride, heated at 70 — 130° , 4 parts of the former are absorbed and a black sublimate is obtained the composition of which corresponds with $7(\text{C}_{10}\text{H}_{15.6}), 2\text{Al}_2\text{Cl}_6$; this substance is insoluble and readily oxidisable; it is decomposed by moisture, yielding a light yellow powder which even after prolonged washing still contains both aluminium and chlorine; when distilled with quick lime, it gives off a mixture of hydrocarbons ($\text{C}_{10}\text{H}_{14}$, $\text{C}_{10}\text{H}_{16}$, and $\text{C}_{10}\text{H}_{18}$) boiling from 150° to 306° . The greater portion of the aluminium chloride and acetylene, however, combine to form a non-volatile, black substance; this product contains less hydrogen than the sublimate, having the empirical formula $7(\text{C}_{20}\text{H}_{15}), \text{Al}_2\text{Cl}_6$; it is very insoluble in the ordinary solvents, reduces permanganate in the cold, and on distillation with quick lime yields a small amount of the hydrocarbons, $\text{C}_{15}\text{H}_{20}$, boiling at 150 — 350° ; the less volatile portions are almost solid and contain anthracene.

G. T. M.

Bromination by means of Aluminium Bromide. By CHARLES POURET (*Compt. rend.*, 1900, 130, 1191—1192).—The following bromides were obtained by the action of aluminium bromide on the corresponding chlorides, the bromination being effected either in a flask or in a sealed tube; bromoform, methyl bromide, methylene bromide, ethyl bromide, ethylene dibromide, ethylidene dibromide, acetylene tetrabromide, and pentabromoethane. H. R. LE S.

Reactivity of the Hydrogen Atoms in Disulphones, Trisulphones, and Tetrasulphones. By ARTHUR KÖTZ (*Ber.*, 1900, 33, 1120—1127).—The dimethyl and diethyl derivatives, $\text{C}_3\text{H}_6\text{:}(\text{SO}_2)_2\text{:CMe}_2$ and $\text{C}_3\text{H}_6\text{:}(\text{SO}_2)_2\text{:CEt}_2$, of tetramethylene-1:3-disulphone, can be obtained by the direct alkylation of the latter as well as by the method of Autenrieth and Wolff (Abstr., 1899, i, 581). Disulphones containing the group $\text{SO}_2\text{:CH}_2\text{:SO}_2\text{:}$ were found to be indifferent to nitrous acid and to diazobenzene hydrate, although the formation of

isonitroso-compounds and hydrazones was looked for. Experiments with acetaldehyde, benzaldehyde, nitrobenzaldehyde, chloral, &c., show that, in general, the $\cdot\text{CH}$ radicle of the disulphones, $\text{CHR}:(\text{SO}_2\text{R}')_2$, is as indifferent towards aldehydes as the $\cdot\text{CH}$ radicle in the compounds $\text{CHR}(\text{CO}_2\text{H})_2$, $\text{CO}_2\text{H}\cdot\text{CHR}\cdot\text{CO}\cdot\text{R}$, $\text{CHPhR}\cdot\text{CN}$, $\cdot\text{CO}\cdot\text{CHR}\cdot\text{CO}\cdot$; similarly, the methylene group in the disulphones, $\text{CH}_2(\text{SO}_2\text{R}')_2$, is less reactive than the methylene groups present in the compounds of which the foregoing substances are R-substitution derivatives. The behaviour of formaldehyde with the disulphones, $\text{CH}_2(\text{SO}_2\text{R})_2$, however, is exceptional, giving rise to *tetrasulphones* of the type $\text{CH}_2[\text{CH}(\text{SO}_2\text{R})_2]_2$; this behaviour is analogous to the interaction of formaldehyde with ethyl malonate (Knoevenagel, *Abstr.*, 1894, i, 570) and with ethyl acetoacetate (*Ber.*, 1893, 26, 1087).

Tetraethyltetrasulphone, $\text{CH}_2[\text{CH}(\text{SO}_2\text{Et})_2]_2$, obtained from methylenediethylsulphone and formaldehyde, in presence of a secondary base such as diethylamine as condensing agent, forms colourless crystals; the analogous *tetrapropyl*- and *tetraisopropyl*-derivatives melt at $156\text{--}157^\circ$ and $129\cdot5^\circ$ respectively; *di-trimethylenetetrasulphone*, $\text{CH}_2\left(\text{CH}\begin{smallmatrix} \text{SO}_2\cdot\text{CH}_2 \\ \text{SO}_2\cdot\text{CH}_2 \end{smallmatrix}\right)_2$, melts above 300° .

The behaviour of trimethylenedisulphone with formaldehyde is exceptional; in presence of diethylamine, hydroxyethylsulphonemethylenesulphinic acid, $\text{OH}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{SO}_2\cdot\text{CH}_2\cdot\text{SO}_2\text{H}$, is formed, but without the condensing agent, heating on the water-bath for 6 hours produces a crystalline substance, $\text{CH}_2\begin{smallmatrix} \text{SO}_2\cdot\text{CH}_2 \\ \text{SO}_2\cdot\text{CH}_2 \end{smallmatrix}$, which melts and decomposes at 238° .

The tetrasulphones are, as a class, sparingly soluble in water, form well-defined crystals, and are indifferent towards cold concentrated sulphuric and nitric acids; they combine with bromine, yielding dibromo-derivatives of the type $\text{CH}_2[\text{CBr}(\text{SO}_2\text{R})_2]_2$, which are decomposed by dilute alkalis, regenerating the original tetrasulphone; *dibromotetraethyltetrasulphone* melts at 176° . Tetrasulphones are not changed when warmed with 15 per cent. aqueous sodium hydroxide, but if heated for several hours at 100° , are resolved into formaldehyde and the disulphone $\text{CH}_2(\text{SO}_2\text{R})_2$. Methyl iodide, in presence of sodium hydroxide, does not yield a methyl derivative of the tetrasulphone, but gives rise to the dimethyl derivative, $\text{CMe}_2(\text{SO}_2\text{R})_2$, of the disulphone initially formed by the action of the alkali. Thus, from tetraethyltetrasulphone, under these conditions, sulphonal is obtained.

In discussing the influence of two sulphone groups on the reactivity of the methylene group to which they are attached, it is shown that the disulphones $\text{CH}_2(\text{SO}_2\text{Et})_2$ and $\text{CHMe}(\text{SO}_2\text{Et})_2$ are practically non-conducting in solution, and therefore, like ethyl malonate, and unlike ethyl acetoacetate, cannot be regarded as weak acids; diethylsulphone-phenylsulphonemethane, $\text{CH}(\text{SO}_2\text{Et}_2)\cdot\text{SO}_2\text{Ph}$, on the other hand, from its conductivity, appears to be a strong monobasic acid. W. A. D.

Action of Chloral on the Chloroacetic Acids. By EMILIO GABUTTI (*Gazzetta*, 1900, 30, 253—257).—Chloral reacts with the chloroacetic acids, yielding the corresponding chloroacetates.

Chloral chloroacetate, $\text{CCl}_3 \cdot \text{CH}(\text{O} \cdot \text{CO} \cdot \text{CH}_2\text{Cl})_2$, which is obtained in about a 50 per cent. yield, is a colourless oil with a pungent, aromatic odour, and is very soluble in ether. The *dichloroacetate*, $\text{CCl}_3 \cdot \text{CH}(\text{O} \cdot \text{CO} \cdot \text{CHCl}_2)_2$, obtained in small yield only, is an oil having an indefinite, aromatic odour; it boils at 230° and dissolves in ether. The *trichloroacetate*, $\text{CCl}_3 \cdot \text{CH}(\text{O} \cdot \text{CO} \cdot \text{CCl}_3)_2$, is formed in small quantity as a colourless oil with a pleasing aromatic odour; it boils at $240\text{--}242^\circ$, and is soluble in ether. T. H. P.

Organic Peroxides. IV. By LUDWIG VANINO and EMIL UHLFELDER (*Ber.*, 1900, 33, 1043—1051. Compare *Abstr.*, 1894, i, 416; 1896, i, 597; 1897, i, 621).—In the preparation of *chloroacetyl peroxide* by von Pechmann and Vanino's method (*Abstr.*, 1894, i, 416), it is advisable to employ sodium acetate instead of sodium hydroxide solution, and to see that the mixture is kept well cooled and thoroughly shaken. It crystallises in small needles, melts at 36° , decomposes at 85° , and dissolves readily in most solvents, with the exception of light petroleum. It explodes under pressure or when struck, but when heated on platinum merely burns; it also explodes when mixed with aluminium, lead peroxide, sulphur, or potassium chlorate. *Trichloroacetyl peroxide* decomposed so readily that it could not be examined in detail.

m-Nitrobenzoyl peroxide (Brodie, *Annalen, Supp.*, 3, 209; Vanino, *Abstr.*, 1897, i, 621) may be obtained by adding benzoyl peroxide to a well cooled mixture of concentrated nitric and sulphuric acids, or by the action of alkaline hydrogen peroxide on an acetone solution of *m*-nitrobenzoyl chloride.

The oxidation of *p*-nitrobenzoyl chloride to the peroxide only takes place when pyridine is employed instead of sodium hydroxide; the *peroxide* forms yellow crystals, melts at 151° , and readily decomposes.

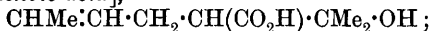
o-Bromobenzoyl peroxide, obtained by the action of hydrogen peroxide and pyridine on the chloride, crystallises in colourless needles, detonates at 114° , and is readily soluble in most organic solvents; the *m*-bromo-compound melts at 132° , and the *p*-bromo-derivative detonates at 152° .

It has not been found possible to isolate *o*-iodobenzoyl peroxide in a state of purity; the crude product melts between 68° and 90° . When this crude product is dissolved in boiling acetic acid and the solution then treated with light petroleum, an acid melting at 228° , and isomeric with Meyer and Wachter's iodosobenzoic acid, is obtained; from hot water, in which it is much more readily soluble than Meyer and Wachter's acid, it crystallises in small needles, and dissolves in alkalis yielding colourless solutions; it does not yield an acetyl derivative when treated with acetic anhydride. The authors suggest that their acid has the constitution $\text{OI} \cdot \text{C}_6\text{H}_4 \cdot \text{CO}_2\text{H}$, and Meyer's acid the constitution $\text{C}_6\text{H}_4 \begin{smallmatrix} \text{I(OH)} \\ \diagup \quad \diagdown \\ \text{CO} \end{smallmatrix} \text{O}$ (compare *Abstr.*, 1892, i, 1460). J. J. S.

Cineolic Acid. By HANS RUPE (*Ber.*, 1900, 33, 1129—1140).—Cineolic acid, when heated with water at 160° for 3 hours, yields a mixture of two isomeric acids, $\text{C}_9\text{H}_{16}\text{O}_3$; the first of these, *cinenic acid*, is stable towards aqueous potassium permanganate, does not interact with bromine, phenylhydrazine, hydroxylamine, or semicarbazide, and

thus appears to have the structure $\text{CHMe} \begin{smallmatrix} \text{CH}_2 \cdot \text{CH}_2 \\ \text{O} - \text{CMe}_2 \end{smallmatrix} \text{CH} \cdot \text{CO}_2\text{H}$.

The second acid, which appears to be formed by the action of water at 160° on cinenic acid, since a yield of 50 per cent. can be obtained in this way from the latter, is a *methoethylol-5-hexene-2-acid-6* [*α -hydroxyisopropyl- $\Delta\gamma$ -hexenoic acid*],



this view of its structure is supported by its decolorising aqueous potassium permanganate, by its combining directly with 1 mol. of bromine, and by its losing water, when heated, in the manner characteristic of β -hydroxy-acids, yielding *methoethene-5-hexene-2-acid-6* [*α -isopropylidene- $\Delta\gamma$ -hexenoic acid*], $\text{CHMe}:\text{CH}:\text{CH}_2:\text{C}(\text{CO}_2\text{H})\cdot\text{CMe}_2$.

Cinenic acid crystallises from light petroleum in beautiful, transparent crystals, melts at $83-84^\circ$, and boils at $127.5-129.5^\circ$ under 14 mm. and at $245-247^\circ$ under atmospheric pressure; whilst *cineolic acid* has $\lambda_{1024} - \lambda_{32} = 27.02$ at 18° , *cinenic acid* has $\lambda_{1024} - \lambda_{32} = 70.03$. The *silver* salt forms slender white needles, and the *calcium* salt (with $2\text{H}_2\text{O}$) a microcrystalline mass; the *methyl* ester is a colourless liquid, which boils at $86-89^\circ$ under 14 mm. pressure, and has a camphor-like odour; the *ethyl* ester boils at $111-113^\circ$ under 17 mm. pressure. When cinenic acid is esterified by passing hydrogen chloride into its alcoholic solution, fission of the ring occurs, and *ethyl δ -chloro- α -methoethylolhexoate*,



is apparently formed; the ester isolated, however, which boiled at $131-136^\circ$, was by no means pure.

α -Hydroxyisopropyl- $\Delta\gamma$ -hexenoic acid crystallises from water in small, white, nacreous leaflets, from light petroleum in matted, silky needles, melts at $59-60^\circ$, and boils at $152-153^\circ$ under 10 mm. pressure; the *silver* salt is amorphous, and the *magnesium* salt (with $2\text{H}_2\text{O}$) microcrystalline. *α -iso-Propylidene- $\Delta\gamma$ -hexenoic acid*, obtained by distilling the foregoing acid under atmospheric pressure, boils at $136-138^\circ$ under 11 mm. pressure, has a sp. gr. 0.9816 at 17° , $\mu_D = 7.48$, a molecular refraction 44.57, and is transparent and colourless; in the air, it gradually becomes yellow and finally resinifies; the *silver* salt is amorphous and unstable, and the *calcium* salt (with $1\text{H}_2\text{O}$) forms sheaf-like aggregates of microscopic needles.

Ethyl hydrogen cineolate, $\text{CO}_2\text{H} \cdot \text{C}_{10}\text{H}_{14}\text{O} \cdot \text{CO}_2\text{Et}$, crystallises from dilute alcohol, or better from petroleum of high boiling point, in slender needles, and melts at $99-100^\circ$. When cineolic acid is heated for several hours at $160-165^\circ$ with 10 per cent. aqueous sulphuric acid, there is formed a considerable amount of the acid $\text{C}_9\text{H}_{16}\text{O}_3$, obtained by Wallach and Gildemeister in very minute quantity by the dry distillation of cineolic acid. The foregoing results accord well with Wallach's formula, $\text{CO}_2\text{H} \cdot \text{CMe} \begin{smallmatrix} \text{CH}_2 \cdot \text{CH}_2 \\ \text{O} - \text{CMe}_2 \end{smallmatrix} \text{CH} \cdot \text{CO}_2\text{H}$, for cineolic acid.

W. A. D.

Preparation of Ethyl β -Alkoxy- α -cyanocrotonates Isomeric with Ethyl Cyanoalkylacetoacetates. By ALBIN HALLER (*Compt. rend.*, 1900, 130, 1221-1225).—*Ethyl β -ethoxy- α -cyanocroto-*

nate, the isomeride of ethyl cyanoethylacetoacetate, is prepared by treating the silver derivative of ethyl cyanoacetoacetate with a slight excess of ethyl iodide on the water-bath; it crystallises from ether in colourless needles melting at 76° , and dissolves in the ordinary organic solvents, but not in water or aqueous solutions of alkali hydroxides. When treated with alcoholic potash, it is hydrolysed into ethyl alcohol and the potassium derivative of ethyl cyanoacetoacetate; with hydrochloric acid, it undergoes a similar decomposition, yielding ethyl chloride and ethyl cyanoacetoacetate.

Ethyl β -amino- α -cyanocrotonate, obtained by treating the preceding compound with aqueous ammonia, separates from alcohol in prismatic crystals and melts at 188° ; it is identical with the compound obtained in small quantities by the action of ammonia on ethyl cyanoacetoacetate itself.

Ethyl β -methoxy- α -cyanocrotonate, produced by employing methyl iodide in the above condensation, crystallises in needles melting at 134° .

The corresponding *β -propyloxy-*, *β -isobutyloxy-*, and *β -benzyloxy-*esters melt at 85 — 86° , 94 , and 113° respectively.

The formation of substituted *β -alkoxycrotonates* from ethyl cyanoacetoacetate raises the question as to whether this substance is not in reality a *β -hydroxy- α -cyanocrotonate*. On the other hand, the tautomeric change may occur when the ester is converted into its metallic derivative.

G. T. M.

Ethyl Acetoacetate. II. By HEINRICH GOLDSCHMIDT and LAZAR OSLAN (*Ber.*, 1900, 33, 1140—1152. Compare this vol., i, 132).—By using a purer preparation of ethyl acetoacetate, the value of the affinity constant at 25° has been reduced from $k = 0.63 \times 10^{-7}$ to $k = 0.4 \times 10^{-8}$, but is probably still too high. By determining the velocity constant of the hydrolysis of the ester by weak bases, the value $k = 2 \times 10^{-11}$ has been obtained. The hydrolytic constant of ethyl sodioacetoacetate is then calculated to be 0.65×10^{-5} .

The hydrolysis of ethyl dimethylacetoacetate by sodium hydroxide is more rapid than that of ethyl acetoacetate, and proceeds in a normal way as a reaction of the second order, the velocity constant being $k = 2.85$ at 25° .

T. M. L.

Acetylation of Ethyl Acetoacetate. By LUDWIG CLAISEN and E. HAASE (*Ber.*, 1900, 33, 1242—1246. Compare Abstr., 1896, i, 557).—Pure ethyl O-acetylacetoacetate, $\text{CH}_3 \cdot \text{C}(\text{OAc}) : \text{CH} \cdot \text{CO}_2\text{Et}$, can readily be prepared by the action of acetyl chloride (freed from hydrogen chloride by distilling over dimethylaniline) on a mixture of ethyl acetoacetate and pure dry pyridine. It boils at 104 — 105° under 10 mm. and at 214 — 216° with slight decomposition, under atmospheric pressure, is insoluble in alkalis, and not readily attacked by them.

Ethyl O-acetyldiacetoacetate, $\text{CH}_3 \cdot \text{C}(\text{OAc}) : \text{C}(\text{OAc}) \cdot \text{CO}_2\text{Et}$, prepared in a similar way, boils at 142 — 144° under 10 mm., but decomposes completely when distilled under atmospheric pressure; it is a pale yellow oil and is decomposed by water and alkalis as readily as acetic anhydride. The isomeric ethyl triacetoacetate, $\text{C}(\text{OAc})_3 \cdot \text{CO}_2\text{Et}$, is not known, and is probably too unstable to exist.

T. M. L.

Action of Ethyl Chloroacetate on Sodioacetylacetone. By F. MARCH (*Compt. rend.*, 1900, 130, 1192—1194).—*Ethyl $\beta\beta$ -diacetylpropionate*, $\text{CHAc}_2 \cdot \text{CH}_2 \cdot \text{CO}_2\text{Et}$, obtained by heating molecular proportions of ethyl chloroacetate and sodioacetylacetone at 150° for 8 hours, is a yellow liquid boiling at $146\text{--}147^\circ$ under 24 mm. pressure, and is insoluble in water, but readily dissolves in alcohol and ether. Its alcoholic solution gives a greyish precipitate with cupric acetate. Its *phenylhydrazone* readily loses 1 mol. of water, giving

ethyl dimethylphenylpyrazoleacetate, $\text{NPh} \begin{array}{c} \text{N}=\text{CMe} \\ | \\ \text{CMe} \cdot \text{C} \cdot \text{CH}_2 \cdot \text{CO}_2\text{Et} \end{array}$

Methyl $\beta\beta$ -diacetylpropionate, obtained in a similar way, is a nearly colourless liquid boiling at $130\text{--}132^\circ$ under 24 mm. pressure. It is readily soluble in ethyl alcohol, methyl alcohol, and ether, but is insoluble in water. H. R. LE S.

Conversion of Dimethylmaleic Anhydride into Dimethylfumaric Acid. By ETTORE MOLINARI (*Ber.*, 1900, 33, 1408—1419).—The normal methyl ester of dimethylmaleic acid distils at 219° , has a sp. gr. 1.1216 at $0^\circ/0^\circ$, and dissolves readily in most organic solvents. The ethyl ester distils at 237° . When either ester is heated for 24 hours at $100\text{--}106^\circ$ with alcohol saturated at 0° with ammonia, a crystalline product, *aminodimethylsuccinimide*, $\text{NH}_2 \cdot \text{CMe} \begin{array}{c} \text{CO} \text{---} \text{NH} \\ | \quad \quad | \\ \text{CHMe} \cdot \text{CO} \end{array}$, is obtained, which crystallises from alcohol in colourless prisms softening at 165° and melting at 168° . From the mother liquors of this amide, crystals of *dimethylfumaramide* melting at 215° may be obtained. When the imide is hydrolysed with barium hydroxide and the solution acidified with sulphuric acid and evaporated, the corresponding

anhydride, $\text{NH}_2 \cdot \text{CMe} \begin{array}{c} \text{CO} \text{---} \text{O} \\ | \quad \quad | \\ \text{CHMe} \cdot \text{CO} \end{array}$, is obtained; it melts at $164\text{--}165^\circ$, dissolves readily in water, but is insoluble in ether, forms monoclinic prismatic crystals [$a:b:c = 0.7955:1:0.5914$; $\beta = 64^\circ 18'$], and when boiled for some time with water yields a small quantity of a crystalline compound which does not melt even at 330° , and is probably the corresponding acid. An *acid barium salt*, $\text{C}_{12}\text{H}_{18}\text{O}_7\text{Ba}$, is obtained when the anhydride is treated with one equivalent of barium hydroxide.

The original mother liquors from the imide, when repeatedly concentrated in a desiccator, yield hard, colourless crystals of *dimethylmaleamide*, which softens at 155° , melts at 161° , and when hydrolysed with barium hydroxide yields a compound free from nitrogen, together with a crystalline compound containing nitrogen.

When the mother liquor from the amide is extracted with ether, it yields a substance identical with the dimethylmaleimide obtained by Weidel and Brix (*Abstr.*, 1882, 1304). From the results of molecular weight determinations, the substance must have the simple formula, although when hydrolysed with barium hydroxide only half the nitrogen is evolved as ammonia. Among the products of hydrolysis is an *acid* isomeric with dimethylmaleic acid; this crystallises in nodular masses composed of small prisms, melts at $151\text{--}152^\circ$, and is regarded by the author as the hitherto unknown dimethylfumaric acid. The same acid

is formed when aminodimethylsuccinic anhydride is treated with methyl iodide and alkali. This conversion of dimethylmaleic anhydride into dimethylfumaric acid is analogous to Körner and Menozzi's conversion of maleic anhydride into fumaric acid. J. J. S.

Formation of Oxalacetic Acid by Oxidation with Potassium Permanganate in Alkaline Solution. By RUDOLPH FITTIG (*Ber.*, 1900, 33, 1295—1296).—By following the procedure of Fenton and Jones (*Trans.*, 1900, 77, 77), the author is now able to obtain appreciable quantities of oxalacetic acid by the oxidation of teraconic acid with potassium permanganate in alkaline solution (compare *Abstr.*, 1899, i, 418). R. H. P.

[Tartar] Emetics. By G. BAUDRAN (*Ann. Chim. Phys.*, 1900, [vii], 19, 536—574).—The most convenient method of preparing tartar emetics having definite physical and chemical properties is by treating the substance produced by the interaction of tartaric acid with a hydrated sesquioxide, prepared in the cold, with a solution of a normal alkali tartrate. Ordinary tartar emetic, when prepared in this way, dissolves in 25 parts of water at 25°, and in 3 parts at 100°, and has $[\alpha]_D + 136^{\circ}4'$.

Bismuth hydrated oxide, $\text{Bi}_2\text{O}_3 \cdot \text{H}_2\text{O}$, readily combines with tartaric acid, yielding *bismuthotartaric acid*, $\text{C}_4\text{H}_5(\text{BiO})\text{O}_6 \cdot \text{H}_2\text{O}$; this substance crystallises in prismatic needles, dissolves in 228 parts of water, and has $[\alpha]_D + 93^{\circ}40'$. The corresponding *emetic*, $\text{C}_4\text{H}_4(\text{BiO})\text{KO}_6 \cdot \frac{1}{2}\text{H}_2\text{O}$, resembles the antimony analogue, and has $[\alpha]_D + 47^{\circ}35'$; unlike the product obtained by Schwarzenberg, it is not decomposed by water.

The *manganese emetic*, $\text{C}_4\text{H}_4(\text{MnO})\text{KO}_6 \cdot \frac{1}{2}\text{H}_2\text{O}$, obtained by dissolving the hydrate $\text{Mn}_2\text{O}_3 \cdot \text{H}_2\text{O}$ in potassium tartrate, and then adding the necessary amount of tartaric acid, separates in pink crystals, and has $[\alpha]_D + 23^{\circ}20'$.

Borotartaric acid, $\text{B}(\text{C}_4\text{H}_5\text{O}_6)_3 \cdot 3\text{H}_2\text{O}$, produced by the action of tartaric acid (3 mols.) on orthoboric acid (1 mol.), forms very soluble, prismatic crystals, and has $[\alpha]_D + 26^{\circ}30'$. The *potassium salt* (boron emetic), $\text{B}(\text{C}_4\text{H}_4\text{KO}_6)_3 \cdot \frac{1}{2}\text{H}_2\text{O}$, prepared either by the general method or by neutralising the preceding acid with potassium hydroxide (3 mols.), is soluble in 16 parts of boiling water, and has $[\alpha]_D + 20^{\circ}50'$.

Ferritartaric acid, $\text{Fe}_2(\text{C}_4\text{H}_5\text{O}_6)_6 \cdot 10\text{H}_2\text{O}$, is obtained in red, prismatic crystals when ferric hydroxide is treated with a cold solution of tartaric acid (6 mols.), and has $[\alpha]_D + 60^{\circ}$; when heated at 100°, it loses water and becomes greenish-yellow; its neutral solutions do not give iron reactions with potassium thiocyanate or ammonium hydrosulphide. *Potassium ferritartrate*, $\text{Fe}_2(\text{C}_4\text{H}_4\text{KO}_6)_6 \cdot \text{H}_2\text{O}$, prepared by methods similar to those employed for the borotartrate, forms yellow crystals, and has $[\alpha]_D + 45^{\circ}$; the *ammonium salt* has $[\alpha]_D + 49^{\circ}50'$.

Aluminotartaric acid, $\text{Al}_2(\text{C}_4\text{H}_5\text{O}_6)_6 \cdot 6\text{H}_2\text{O}$, obtained like the corresponding ferric derivative, crystallises in prisms, dissolves in its own weight of water, and has $[\alpha]_D + 20^{\circ}$; its *potassium salt*, $\text{Al}_2(\text{C}_4\text{H}_4\text{KO}_6)_6 \cdot \text{H}_2\text{O}$, has $[\alpha]_D + 23^{\circ}20'$.

Chromotartaric acid, like the aluminium compound, crystallises with $6\text{H}_2\text{O}$, and its *potassium salt* crystallises with $1\text{H}_2\text{O}$; green and violet

modifications of these compounds have been obtained, the former being the more stable in the case of the salt, and the latter in that of the acid. G. T. M.

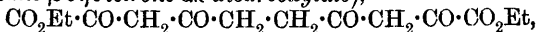
General Observations on "Emetics." By L. LÉON A. PRUNIER (*Bull. Soc. Chim.*, 1900, [iii], 23, 101—103).—A short account of Baudran's work (preceding abstract), with a view to the discussion of its theoretical significance. N. L.

Some Racemic Substances. By J. SCHLOSSBERG (*Ber.*, 1900, 33, 1082—1087).—By adding to saturated solutions of the following inactive salts or acids at 20° some of the corresponding *d*-salts or acids (in the case of tropic acid the *l*-acid), and finding that the amount dissolved was increased thereby, and that the solution acquired a slight optical activity, it was shown that the inactive substances in question exist at 20° as racemic compounds: *sodium lithium racemate*, $C_4H_4O_6NaLi \cdot 2H_2O$ (*d*-tartrate, $C_4H_4O_6NaLi \cdot H_2O$); *potassium sodium racemate*; *ammonium lithium racemate* (*d*-tartrate, $C_4H_4O_6(NH_4)Li \cdot \frac{1}{2}H_2O$); *potassium sodium racemate*; *inactive potassium pyrotartrate*, $C_5H_6O_6K_2 \cdot H_2O$; *inactive sodium pyrotartrate*, $C_5H_6O_6Na_2 \cdot 6H_2O$; *tropic acid*; *mandelic acid* (compare Rimbach, *Abstr.*, 1899, i, 895).

C. F. B.

Preparation of Acetonylacetone. By LUDWIG KNORR (*Ber.*, 1900, 33, 1219).—Ethyl diacetylsuccinate, when boiled for 1 hour with 20 per cent. aqueous potassium carbonate, gives an 80 per cent. yield of acetonylacetone; the latter boils at 191°, 178°, and 137° under pressures of 750, 500, and 150 mm. respectively. It has a sp. gr. 0.973 at 20°/4°, μ_D 1.428 at 20°, and a molecular refraction 30.14, that calculated for the keto-formula being 30.10, and for the enolic formula 31.98. W. A. D.

Syntheses with Acetonylacetone. I. By THOMAS GRAY (*Ber.*, 1900, 33, 1220—1223).—Acetonylacetone combines with diethyl oxalate in presence of sodium to form *diethyl acetonylacetonedioxalate* (*diethyl decane- $\beta\delta\eta$ -tetrone- $\alpha\kappa$ -dicarboxylate*),



which crystallises from alcohol in nearly colourless, lustrous, rhombohedral leaflets, melts at 100—101°, and with alcoholic hydrazine hydrate yields symmetrical *di-3-carboxethylpyrazyl-5-ethane*

[*ethyl ethane-bis-5-pyrazyl-3-carboxylate*], $C_2H_4 \left(C \begin{array}{c} \text{CH} \cdot C \cdot CO_2Et \\ \diagdown \quad \diagup \\ NH \cdot N \end{array} \right)_2$; this

crystallises from alcohol in rhombohedral leaflets, melts at 198—199°, and, on hydrolysis, yields the corresponding *dicarboxylic acid*, $C_{10}H_{10}O_4N_4$, as a crystalline powder. The latter melts at 309—310°, and is thereby converted into *5-dipyrazylethane*, $C_2H_4 \left(C \begin{array}{c} \text{CH} \cdot \text{CH} \\ \diagdown \quad \diagup \\ NH \cdot N \end{array} \right)_2$,

which crystallises from dilute alcohol in spindle-shaped crystals, and melts at 150—151°; on oxidation with alkaline potassium permanganate, the acid yields pyrazole-3:5-dicarboxylic acid (Knorr and Macdonald, *Abstr.*, 1894, i, 543).

The alternative formula, $\text{CO}_2\text{Et}\cdot\text{CO}\cdot\text{CHAc}\cdot\text{CHAc}\cdot\text{CO}\cdot\text{CO}_2\text{Et}$, for the condensation product of acetonylacetone with diethyl oxalate is excluded by the foregoing facts.

W. A. D.

Oxidation of Erythritol by the Sorbose Bacterium. Production of Erythrulose, a new Sugar. By GABRIEL BERTRAND (*Compt. rend.*, 1900, 130, 1330—1333. Compare Abstr., 1898, i, 550, 556).—*Erythrulose*, $\text{OH}\cdot\text{CH}_2\cdot\text{CO}\cdot\text{CH}(\text{OH})\cdot\text{CH}_2\cdot\text{OH}$, is produced by allowing a culture of the sorbose bacterium to develop in a decoction of yeast and erythritol; after three weeks, when the polyhydric alcohol is completely oxidised, the solution is freed from zooglea, neutralised with a solution of barium hydroxide, and evaporated under diminished pressure, the sugar being obtained as an uncrystallisable syrup. Like its lower homologue dihydroxyacetone, erythrulose readily reduces Fehling's solution, even in the cold, combines with sodium hydrogen sulphite, and is easily soluble in a mixture of alcohol and ether; it has a specific rotation $+12^\circ$, and is non-fermentable. Its hydrazones, produced by the action of phenylhydrazine, bromophenylhydrazine, and phenylbenzylhydrazine in cold solutions, are all extremely soluble, and could not be isolated. In warm dilute acetic acid solutions, the osazones are formed; *phenylerythrulosazone*, $\text{C}_{16}\text{H}_{18}\text{O}_2\text{N}_4$, crystallises in golden-yellow needles, melts at 174° , has a specific rotation $+50^\circ$, and is very soluble in alcohol and acetone; *p-bromophenylerythrulosazone*, $\text{C}_{16}\text{H}_{16}\text{N}_4\text{Br}_2\text{O}_2$, is somewhat less soluble than the preceding compound, and melts at $194\text{--}195^\circ$. The new sugar is very stable towards aqueous solutions of bromine; its aldehydic isomerides (Wohl, this vol., i, 140), on the contrary, yield monobasic acids containing four carbon atoms. Further investigations are being conducted, with a view of ascertaining whether erythrulose belongs to the *d*- or the *l*-series, or whether it is a mixture containing unequal proportions of both modifications.

G. T. M.

Pentoses and Methylpentoses. By SULEIMAN BEY (*Chem. Centr.*, 1900, i, 803—804; from *Zeit. klin. Med.*, 39, 305—312).—*Barium dixylosate*, $\text{BaO}(\text{C}_5\text{H}_{10}\text{O}_5)_2$, separates as a white, amorphous precipitate when a hot, saturated solution of barium hydroxide is added to an alcoholic solution of xylose, or when barium hydroxide is dissolved in a solution of xylose at the ordinary temperature, and the filtrate poured into 96 per cent. alcohol at 0° . The composition of this precipitate, unlike those similarly prepared from dextrose, lævulose, sucrose, and lactose, is not dependent on the relative proportions of barium hydroxide, alcohol, or xylose. Xylose may be completely precipitated from aqueous solutions in this form, and its amount estimated with accuracy. On keeping, the dry compound gradually becomes canary-yellow, whilst the strontium salt, which is similarly prepared, turns reddish-yellow. Calcium dixylosate is not precipitated by alcohol from solutions containing less than 30 per cent., and arabinose and xylose behave in this respect like dextrose and sucrose. Barium and strontium diarabinosates are prepared in a similar way to the dixylosates, but both compounds are very unstable. The barium pentosates are completely decomposed by carbon dioxide, the carbo-

hydrates being liberated in a state of purity, whilst, under similar conditions, only 3—5 per cent. of the corresponding saccharate is attacked.

E. W. W.

Compounds of Fructose (Lævulose) with the Haloid Salts of the Alkaline Earths; Oxidation of Fructose. By ROBERT H. SMITH and BERNHARD TOLLENS (*Ber.*, 1900, 33, 1277—1285).—The compound, $C_6H_{12}O_6 \cdot CaBr_2 \cdot 4H_2O$, is obtained when bromine is added to an aqueous solution of lævulose in which precipitated calcium carbonate is suspended, and forms a white, crystalline mass; it can also be obtained from lævulose and calcium bromide, and is very soluble in water, but is not deliquescent. In water, it has at first a specific rotation $[\alpha]_D + 40.25^\circ$ and a constant specific rotation $[\alpha]_D - 36.54^\circ$; if, however, these values are recalculated according to the amount of lævulose in the solutions examined, values of $[\alpha]_D$ are obtained practically coinciding with those for lævulose, thus showing that the additive compound is decomposed by water. The compound, $(C_6H_{12}O_6)_2 \cdot CaCl_2 \cdot 2H_2O$, is obtained in a similar manner, and has a specific rotation $[\alpha]_D - 64.5^\circ$. The compound, $(C_6H_{12}O_6)_2 \cdot CaI_2 \cdot 2H_2O$, forms a hard, deliquescent mass, and shows a constant specific rotation $[\alpha]_D - 47.4^\circ$. The compound, $(C_6H_{12}O_6)_2 \cdot SrCl_2 \cdot 3H_2O$, is very stable in air, and shows a constant specific rotation $[\alpha]_D - 57.6^\circ$. The compound, $(C_6H_{12}O_6)_2 \cdot SrBr_2 \cdot 3H_2O$, forms stable, transparent, tabular crystals, and shows a constant specific rotation $[\alpha]_D - 49.9^\circ$. The compound, $(C_6H_{12}O_6)_3 \cdot (SrI_2)_2 \cdot 4H_2O$, forms a very hard mass, and the compound, $(C_6H_{12}O_6)_2 \cdot BaI_2 \cdot 2H_2O$, is deliquescent. On mixing solutions of lævulose and these haloid salts, heat is generally developed, and 1 mol. of lævulose seems to replace 2 mols. of water of crystallisation.

The authors confirm Kiliani's statement (*Ber.*, 1882, 14, 2530) that lævulose, on oxidation with nitric acid, yields mesotartaric acid and small quantities of glycollic acid.

R. H. P.

Polarisation and Reducing Power of Sorbose. By ROBERT H. SMITH and BERNHARD TOLLENS (*Ber.*, 1900, 33, 1285—1293).—The specific rotation of sorbose in aqueous solution can be calculated from the formula $[\alpha]_D = -(42.65 + 0.047p + 0.00007p^2 - [t - 20]0.02)^\circ$, where p is the percentage concentration and t the temperature.

It was found that sorbose would reduce far less Fehling's solution than the same weight of dextrose under equal conditions, and a formula is given showing the reducing power of sorbose. R. H. P.

Variation of the Specific Rotation of Sucrose with the Temperature. By OTTO SCHÖNROCK (*Zeit. Ver. Deut. Zuck.-Ind.*, 1900, 413—434).—An elaborate series of experiments leads to the following expression for the variation of the specific rotation of sucrose in solutions containing about 26 grams per 100 c.c. for temperatures lying between 10° and 32° . $[\alpha]_D^t = [\alpha]_D^{20^\circ} - [\alpha]_D^{20^\circ} \cdot 0.000217 (t - 20)$, where $[\alpha]_D^t$ is the specific rotation at the temperature t . T. H. P.

Stability of Sucrose Solutions. By WILLIAM OECHSNER DE CONINCK (*Compt. rend.*, 1900, 130, 1261—1263. Compare this vol., i, 236).—A current of dry, sterilised air produces no alteration in a

sterilised aqueous solution of sucrose protected from light, even when the experiment is continued for a fortnight. If ordinary air is allowed to enter, the dissolved sugar rapidly becomes inverted; at the same time, moulds develop in the solution and fermentation sets in attended by the formation of ethyl alcohol and carbon dioxide. Acetaldehyde, glycol, glycerol, oxalic and succinic acids could not be detected in the fermented solution. G. T. M.

Gum Tragacanth. By ALBERT HILGER and W.-E. DREYFUS (*Ber.*, 1900, 33, 1178—1191).—Five different samples of gum tragacanth were found to contain 15.4—9.4 per cent. of water, and 3.1—2.7 of ash; also 15.1—22.4 of galactose (estimated as mucic acid), and 42—30 per cent. of arabinose (estimated as furfuraldehyde phenylhydrazone). The samples obtained by artificial incision of the plant contain the larger quantities of water and ash. A sample of vermicelli tragacanth ("Fadentragant") contained 4 per cent. of cellulose and 3 of starch; allowing for these, the tragacanth proper is found to have the composition of a polysaccharide, $C_{11}H_{20}O_{10}$, for which the name bassorin should be reserved; this is quite insoluble in water. When the gum is boiled for 30 hours with 2 per cent. sulphuric acid, arabinose can be isolated from the product, but no other crystalline substance; the mother-liquors, however, yield mucic acid on oxidation. When it is allowed to remain 2—3 days in 35 per cent. potassium hydroxide, and the alkaline solution precipitated with glacial acetic acid, oxybassorin, $(C_{11}H_{20}O_{10})_2O$, is obtained. If the alkaline solution is neutralised with dilute acetic acid and precipitated with alcohol, a potassium derivative of oxybassorin is obtained; this is soluble in water and yields insoluble copper and silver derivatives by double decomposition. These compounds do not give the usual reactions of the metals, and cannot be regarded as true salts. The potassium derivative has the character of a simple sugar; it is strongly dextrorotatory, and reduces Fehling's solution and ammoniacal silver solution, but not Soldani's reagent, and does not restore the colour to magenta solution decolorised with sulphurous acid. Sodium amalgam reduces an alkaline solution of oxybassorin to an optically inactive substance without reducing properties. C. F. B.

Some New Tellurium Compounds. By VICTOR LENHER (*J. Amer. Chem. Soc.*, 1900, 22, 136—141).—Tellurium tetrabromide and tetrachloride readily unite with the corresponding halogen salts of both aliphatic and aromatic amines to form well-crystallised double salts of the composition $(B'HB r)_2, TeBr_4$ and $(B'HCl)_2, TeCl_4$. The bromides are invariably red, and the chlorides yellow. They are all soluble in dilute acids and in alcohol, but are decomposed by pure water with the formation of hydrated tellurium dioxide. The following salts are described: the telluribromides of ethylamine, trimethylamine, aniline, pyridine, and quinoline, and the tellurichlorides of methylamine, ethylamine, aniline, pyridine, and quinoline.

A solution of tellurium dioxide in halogen acids also yields a precipitate with most of the alkaloids. E. G.

Bewad's Triethylamine Oxide. By ARTHUR LACHMAN (*Ber.*, 1900, 33, 1030—1034. Compare Abstr., 1899, i, 326).—The author has prepared further quantities of Bewad's triethylamine oxide (Abstr., 1888, 112, 1127) by the method previously described, and from a study of the reactions of the compound, comes to the conclusion that it resembles the hydroxylamines, especially diethylhydroxylamine, and its isomerism with Dunstan and Goulding's compound thus becomes even more difficult to explain.

The hydrochloride forms large, extremely hygroscopic crystals. The base, when boiled at atmospheric pressure, undergoes partial decomposition; it reacts with methyl iodide, iodine being liberated, and triethylamine hydriodide formed. No condensation products could be obtained with either aniline or phenylhydrazine. It readily reduces dichromate, permanganate, Fehling's solution, ammoniacal silver nitrate, and sodium nitrite. J. J. S.

Diethylhydroxylamine. By ARTHUR LACHMAN (*Ber.*, 1900, 33, 1022—1030. Compare Dunstan and Goulding, *Trans.*, 1899, 75, 792).—In most syntheses with zinc alkyls, two alkyl groups can only be introduced into the molecule when 2 mols. of the reagent are employed. With diphenylnitrosamine, however, two ethyl groups are introduced, and diethylhydroxylamine is formed when only 1 mol. of zinc ethyl is employed. Dimethyl- and diethyl-nitrosamine, on the other hand, do not react with zinc ethyl. Special precautions are required in the isolation of the diethylhydroxylamine, for which the original must be consulted.

After extraction with ether, it is most readily purified by fractional distillation under about 100 mm. pressure, the yield being usually about 30 per cent. The pure base forms a colourless, oily liquid with a characteristic aromatic odour, boils at 47—49° under 15 mm., 79—80° under 100 mm., and 130—135° under 750 mm. pressure, but with some decomposition in the last case, has a sp. gr. 0.8784 at 15°/15°, and dissolves readily in all solvents with the exception of light petroleum. Its aqueous solution precipitates lead, copper, zinc, and aluminium salts, but not those of magnesium, cobalt, or nickel, and in addition has strong reducing properties. The *hydrochloride*, $C_4H_{11}ON \cdot HCl$, forms white, crystalline scales, melting indefinitely at 55—65°. *Triethylhydroxylammonium iodide*, $OH \cdot NEt_3I$, formed by the direct union of ethyl iodide and diethylhydroxylamine, crystallises in needles, softens at 40°, but has no fixed melting point; it is extremely hygroscopic, and is insoluble in benzene, ether, or light petroleum; when reduced, it yields triethylamine, and when heated triethylamine, triethyloxamine, iodine, and water.

Triethyloxamine platinichloride (compare Dunstan and Goulding, *loc. cit.*) crystallises from water with $2H_2O$. J. J. S.

Quinquevalent Nitrogen. By ARTHUR LACHMAN (*Ber.*, 1900, 33, 1035—1040. Compare Abstr., 1898, i, 400).—The following are the more important generalisations brought forward by the author.

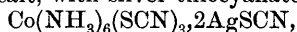
No quinquevalent nitrogen derivatives are known in which the five radicles are of the same chemical nature; one or more of the radicles

must be of an opposite chemical nature, but not too pronounced. An increase of temperature tends to convert a quinque- into a ter-valent derivative; this is most pronounced when two of the five radicles are of opposite chemical nature to the remaining three.

Certain nitro-derivatives, for example, nitrobenzene, contain ter-valent nitrogen; others, for example, nitroethane, quinquivalent nitrogen.

J. J. S.

Ammonio-cobalt Thiocyanates. By ARTURO MIOLATI (*Zeit. anorg. Chem.*, 1900, 240—244).—*Luteocobalt thiocyanate*, $\text{Co}(\text{NH}_3)_6(\text{SCN})_3$, is obtained by adding barium thiocyanate to a solution of luteocobalt sulphate containing a small quantity of sulphuric acid, and evaporating the filtrate in a vacuum over sulphuric acid; it crystallises in orange-yellow, lustrous tablets, is decomposed by hot water, and can be recrystallised from a solution of magnesium thiocyanate. The *double salt*, with mercury thiocyanate, $\text{Co}(\text{NH}_3)_6(\text{SCN})_3 \cdot 2\text{Hg}(\text{SCN})_2$, obtained by heating a solution of the preceding salt with mercury thiocyanate, crystallises in beautiful, golden leaflets, is decomposed by water, and can be recrystallised from a solution of ammonium thiocyanate. The *double salt*, with silver thiocyanate,



crystallises in lustrous, yellow leaflets, and is decomposed by water. The *double salt*, with platinum thiocyanate, is an orange-yellow, micro-crystalline precipitate, and is decomposed by hot water. These double salts do not correspond in composition to those obtained from luteocobalt chloride or luteochromium chloride and mercury chloride, but are analogous to the complex fluorides, $\text{Co}(\text{NH}_3)_6\text{F}_3 \cdot 2\text{SiF}_4$, &c., previously described by Miolati and Rossi (*Abstr.*, 1898, ii, 222).

E. C. R.

Double Thiocyanates. By ARTHUR ROSENHEIM and ROBERT COHN (*Ber.*, 1900, 33, 1111—1114).—*Mercury bromothiocyanate*, $\text{HgBr} \cdot \text{SCN}$, crystallises in beautiful needles and is insoluble in water, but dissolves unchanged in hot alcohol.

Ammonium and *barium* salts of the type $\text{M}'\text{Hg}(\text{SCN})_3$, and *potassium*, *sodium*, *barium*, and *copper* salts of the type $\text{M}'_2\text{Hg}(\text{SCN})_4$ were prepared, the former class being sparingly, the latter easily, soluble in water.

Cobalt yields salts of the type $\text{M}'_2\text{Co}(\text{SCN})_4$, which form dark blue crystals, and are easily soluble in water; the *potassium* and *ammonium* (each with $4\text{H}_2\text{O}$) and the *sodium* and *barium* (each with $8\text{H}_2\text{O}$) salts were analysed. The corresponding crystalline *nickel* salts are green; the *sodium* compound, $2\text{NaSCN} \cdot \text{Ni}(\text{SCN})_2 \cdot 8\text{H}_2\text{O}$, has a normal, but the *potassium* salt, $4\text{KSCN} \cdot \text{Ni}(\text{SCN})_2 \cdot 4\text{H}_2\text{O}$, an abnormal, composition. It is noteworthy that, in alcoholic solution, the cobalt of the cobalt salts is present in the anion $\text{Co}(\text{SCN})_4$, and is deposited on the anode; the nickel of the nickel salts, however, is deposited at the cathode.

The crystalline *aluminium* salt, $\text{Al}(\text{SCN})_3 \cdot 6\text{K}_2\text{O} \cdot 4\text{H}_2\text{O}$, prepared by the action of thiocyanic acid on freshly precipitated aluminium hydroxide in presence of potassium thiocyanate, is easily soluble in water; the corresponding chromium salt (Rösler, *Annalen*, 1867, 141, 185) can be prepared in a similar way.

W. A. D.

New Organo-metallic Compounds of Magnesium and their Application to the Synthesis of Alcohols and Hydrocarbons. By V. GRIGNARD (*Compt. rend.*, 1900, 130, 1322—1324. Compare Barbier, *Abstr.*, 1899, i, 323).—Magnesium turnings act on methyl iodide with extreme slowness, but if anhydrous ether is added a vigorous reaction sets in and the metal dissolves completely, giving rise to a clear, almost colourless, liquid. On distilling off the ether, a grey, semi-crystalline residue is obtained which rapidly deliquesces with an appreciable rise of temperature. When an aldehyde or ketone is added to the ethereal solution, it readily combines with the magnesium compound $\text{MgMeI} + \text{RCHO} = \text{R}\cdot\text{CHMe}\cdot\text{O}\cdot\text{MgI}$, and the product, when treated with dilute acid, furnishes a secondary or tertiary alcohol, $\text{RCHMe}\cdot\text{O}\cdot\text{MgI} + \text{H}_2\text{O} = \text{MgI}\cdot\text{OH} + \text{R}\cdot\text{CHMe}\cdot\text{OH}$, the yield being about 70 per cent. of the theoretical. The reaction is perfectly general for all alkyl iodides and bromides up to the C_6 series. A similar result is produced with benzyl chloride, but the yield is much less owing to the formation of dibenzyl. The following alcohols have been prepared for the first time.

Phenylisobutylcarbinol, $\text{C}_4\text{H}_9\cdot\text{CHPh}\cdot\text{OH}$, from benzaldehyde and *iso*-butylbromide, is a colourless, viscid liquid boiling at 122° under 9 mm. pressure.

Phenyl dimethylcarbinol, $\text{CMe}_2\text{Ph}\cdot\text{OH}$, from acetophenone and methyl iodide, is a colourless liquid with an agreeable odour; it boils at $93\text{--}95^\circ$ under 10 mm. pressure.

Benzyl dimethylcarbinol, $\text{CH}_2\text{Ph}\cdot\text{CMe}_2\cdot\text{OH}$, from acetone and benzyl bromide, is a colourless, somewhat viscid liquid boiling at $103\text{--}104^\circ$ under 10 mm. pressure.

When unsaturated aldehydes or ketones are employed which have their double linkings near the carbonyl group, then the alcohols which are formed at first become dehydrated and olefine hydrocarbons are produced.

$\beta\delta$ -dimethyl- $\Delta^{\beta\delta}$ -pentadiene, $\text{CMe}_2\cdot\text{CH}\cdot\text{CMe}\cdot\text{CH}_2$, obtained from mesityl oxide and methyl iodide, boils at $92\text{--}93^\circ$ under 750 mm. pressure.

G. T. M.

Chemistry of Mercury. II. Mercuric Salts of Ketonic Acids, and Conversion of these into Mercurioketonic Acids. By HEINRICH LEY (*Ber.*, 1900, 33, 1010—1014. Compare *Abstr.*, 1899, ii, 485).—*Mercuric lævulate*, $\text{Hg}(\text{C}_5\text{H}_7\text{O}_3)_2$, crystallises in characteristic silvery plates, and has the molecular conductivity μ 7.88 ($v = 64$), μ 12.54 ($v = 128$). Aqueous sodium hydroxide added to a solution of the salt produces a yellow precipitate of mercuric hydroxide, which dissolves in excess of the reagent, yielding a solution from which acetic acid precipitates a white, gelatinous mass; this is apparently a mixture of the *mercurilævulic* acids, $\text{C}_5\text{H}_6\text{O}_3\text{Hg}$ and $\text{C}_5\text{H}_4\text{O}_3\text{Hg}_2$, and yields lævulic acid when decomposed by hydrogen sulphide.

A similar reaction is given by pyruvic, *β -acetoisobutyric*, and acetonedicarboxylic acids. Crotonic acid also yields a mercuri-compound, the formation of which is probably favoured by the presence of the ethylene linking.

A. H.

Mercurbide, $C_2H_2O_4Hg_6$. By KARL A. HOFMANN (*Ber.*, 1900, 33, 1328—1339. Compare *Abstr.*, 1898, i, 635).—The compound $OHg_2 \cdot C(Hg \cdot OH) \cdot C(Hg \cdot OH) \cdot OHg_2$, formerly described (*loc. cit.*) by the author as an oxymercarbide, is now proved to be a derivative of ethane; it is best prepared by the action of yellow mercuric oxide and aqueous alkali on ethyl alcohol; the base is also obtained, although in smaller yield, if acetaldehyde, propyl alcohol, allyl alcohol, amyl alcohol, cellulose, starch, or sucrose are used in place of ethyl alcohol. It differs from all other organic mercury compounds by its great stability towards hot concentrated alkali and acids, permanganate, chromic acid, alkali hypochlorites and hypobromites, nitrohydrochloric acid, sulphurous acid, hydroxylamine, and dilute hydrazine solution; at high temperatures, it loses water, and an orange-red, explosive *compound*, $C_2O_3Hg_6$ (?), is formed. By heating the base (1 mol.) with ethyl iodide (6 mols.) in ethereal solution, the *iodide*, $C_2I_6Hg_6$, is obtained as a crystalline compound of an intense reddish-yellow colour, insoluble in water, alcohol, or ether. The mercarbide acts on aqueous potassium haloids with liberation of alkali; with potassium chloride, a *chloride*, $C_2O_2Cl_2Hg_6$, is formed, and this, with potassium iodide solution, gives an intense orange-yellow, basic *iodide*. The base forms a white *perchlorate*, $C_2O_2Hg_6(ClO_4)_2$, which, when heated or rubbed, explodes and emits a green light. With sodium hydrogen sulphite solution, the mercarbide gives a bright yellow *substance*, which is turned grey by the action of light, and from which the base is regenerated by heating with nitric acid and then with sodium hydroxide. On digesting the mercarbide *nitrate*, $C_2O_2Hg_2(NO_3)_2$, with ammoniacal ammonium nitrate solution, the *compound*, $C_2O_2Hg_6(NH_3)_2(NO_3)_2$, is obtained, whilst the chloride gives a yellowish-white *powder* of the composition $C_2O_2Cl_2Hg_6(NH_3)_2$ when treated with ammoniacal ammonium chloride solution. Hydrogen sulphide gives, with the mercarbide, a white *sulphide*, and hydrazine hydrate slowly reduces the base, nitrogen and ethane being evolved and mercury deposited.

[With E. EICHWALD.]—The yellow, slightly explosive cyanide, $C_2Hg_4(CN)_2$ (*loc. cit.*), obtained by the action of potassium cyanide on the nitrate of the mercarbide, is not acted on by ammonia, but with hydrogen sulphide gives a white *compound*, $C_2H_2Hg_4S_2$, insoluble in water, alcohol, or ether; with hot 10 per cent. hydrochloric acid, the cyanide yields the *chloride* $(CHCl_2Hg_2)_2$. On boiling the latter with concentrated hydrochloric acid, it is converted into a volatile, strongly-smelling, poisonous compound, $C_2H_4Cl_2Hg_2$, which crystallises in colourless, rectangular leaflets, showing very slight double refraction, and melting at about 173° ; it is readily soluble in alcohol, ether, or water, and from its aqueous solution potassium iodide precipitates slender, white needles of an *iodide*, which crystallises from alcohol or ether in quadratic, optically inactive plates; with the hydrochloric acid solution of the chloride, hydrogen sulphide gives a *sulphide* separating from alcohol in white crystals.

The action of mercuric oxide and alkali on alcohol yields, besides mercarbide, an intermediate product, *trimercuriacetic* acid; it exists

in two modifications, one soluble and the other insoluble in alkali, and gives a *nitrate*, $\text{NO}_3\text{Hg}\cdot\text{C}(\text{Hg}\cdot\text{OH})_2\cdot\text{CO}_2\text{H}$.

[With W. BOSCH.]—On heating the insoluble trimercuriacetic acid with sodium ethoxide and alcohol, it is partly converted into the soluble form, and partly resolved into the mercarbide and oxalic acid; an alkaline solution of the acid is decomposed by permanganate, carbon dioxide being evolved, and the mercarbide formed; heating with mercuric oxide and sodium hydroxide solution also converts the trimercuriacetic acid into mercarbide.

[With JULIUS SAND.]—On extracting the product of the action of methylalcoholic potash and mercuric oxide on potato-starch with nitric acid, besides the nitrate of the mercarbide, another *nitrate* of the composition $\text{C}_3\text{H}_6\text{O}_2\text{Hg}_2\cdot\text{NO}_3$ is obtained, whilst in the case of sucrose, a somewhat similar *compound* of the formula $\text{C}_3\text{H}_6\text{O}_6\text{Hg}_4\cdot\text{NO}_3$ is formed.

T. H. P.

Behaviour of Mercuric Salts towards Olefines. By KARL A. HOFMANN and JULIUS SAND (*Ber.*, 1900, **33**, 1340—1353).—By the action of ethylene on solutions of mercuric salts, compounds of the following kinds are obtained. 1. Ethenemercury salts, $\text{CH}_2\cdot\text{CH}\cdot\text{HgX}$. 2. Ethanolmercury salts, $\text{OH}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{HgX}$. 3. Ethyl ether mercury salts, $\text{O}(\text{CH}_2\cdot\text{CH}_2\cdot\text{HgX})_2$. 4. Polymerised ethenemercury salts, $(\text{C}_2\text{H}_3\text{HgX})_n$. The formation of all these compounds is explained on the supposition that the mercury salt HgX_2 splits up into the ions X and HgX , which then combine with the ethylene, converting it into the saturated compound $\text{XHg}\cdot\text{CH}_2\cdot\text{CH}_2\text{X}$. If this then loses the elements of hydrogen haloid, ethenemercury salts are obtained, whilst if it undergoes hydrolysis, ethanolmercury salts result; if the hydrolysis is only partial, condensation of the product of hydrolysis and the original compound, with loss of hydrogen haloid, gives rise to compounds of type 3. Strong acids, especially hydrochloric, readily decompose all these compounds into ethylene and mercury salt.

On passing ethylene into aqueous mercuric chloride, the *double salt*, $\text{OH}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{HgCl}\cdot\text{HgCl}_2$, is precipitated, together with fine spangles of the compound $\text{C}_6\text{H}_{10}\text{O}_4\text{Cl}_4\text{Hg}_4$, which is the *chloride* corresponding with the *sulphate*, $\text{C}_6\text{H}_{10}\text{O}_{12}\text{S}_2\text{Hg}_4$, obtained by precipitating mercuric sulphate solution by means of ethylene. The double chloride is only slightly soluble in water, but crystallises from alcohol in brilliant plates; it is decomposed by potassium cyanide or strong acids (not acetic), whilst hydrogen sulphide slowly precipitates all the mercury. Potassium hydroxide solution precipitates half the mercury as oxide, and by passing carbon dioxide into the alkaline solution the free ethanol derivative is obtained. The latter is best prepared by adding potassium hydroxide to mercuric nitrate solution until a precipitate persists, ethylene being then passed through until the liquid is clear; more alkali is added, and ethylene again passed through the solution, this process being repeated until a clear alkaline liquid remains. To this, potassium chloride or bromide is added in the proportion of 1 mol. to each atom of mercury present, the passage of carbon dioxide through the liquid then causing the precipitation of

the crystalline ethanolmercury salt. The *chloride*, $\text{OH}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{HgCl}$, melts at 155° , and the *bromide* at 158° . The latter, which forms with ammonia a crystalline compound, $\text{OH}\cdot\text{C}_2\text{H}_4\cdot\text{HgBr}\cdot\text{NH}_3$, melting at 150° , is oxidised by bromine in alkaline solution to *monobromomercuri-acetic acid*, $\text{HgBr}\cdot\text{CH}_2\cdot\text{CO}_2\text{H}$, which separates as a white precipitate, gradually becoming crystalline. The last-named acid, which is obtained in better yield by the action of bromine on an alcoholic solution of mercuric bromide, does not give up its bromine when treated with alkali, nor is it decomposed by 20 per cent. nitric acid, dilute hydrochloric acid, or ammonia, but the addition of potassium iodide converts it into a yellow *iodo-compound*.

The addition of potassium iodide to the solution of ethylene in gradually neutralised mercuric nitrate gives rise, not to an ethanol-derivative, but to *ethenemercury iodide*, $\text{CH}_2\cdot\text{CH}\cdot\text{HgI}$, which separates from methyl alcohol in beautiful, silvery plates melting at 147° ; it is readily soluble in hot alcohol, and suffers decomposition by the action of hydrochloric acid or potassium cyanide. On boiling with mercuric oxide and caustic potash, it is converted into the white dimercuriacetic acid insoluble in alkali. The iodide is readily dissolved by sodium ethoxide, or by an aqueous or alcoholic solution of an equivalent quantity of potassium hydroxide, whilst it is decomposed, with formation of mercuric iodide and an olefine, by the action either of methyl iodide or of iodine in presence of water.

Ethenemercury nitrate, $\text{CH}_2\cdot\text{CH}\cdot\text{HgNO}_3$, obtained by the action of methyl alcoholic silver nitrate on ethanolmercury chloride, separates in spherical aggregates of thin, white, sparkling, doubly-refracting leaflets, which, on heating, give a slight explosion with evolution of reddish vapour. It is readily soluble in water, and the addition of a little dilute hydrochloric acid to the aqueous solution precipitates ethanolmercury chloride, which is decomposed by excess of acid.

Ethanolmercury sulphide, $(\text{OH}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{Hg})_2\text{S}$, is a white, crystalline substance, and the corresponding *hydrosulphide*, $\text{OH}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{HgSH}$, crystallises from water in beautiful spangles.

Ethyl ether mercury chloride, $\text{O}(\text{CH}_2\cdot\text{CH}_2\cdot\text{HgCl})_2$, forming a white, granular, crystalline precipitate melting indefinitely at about 190° ; the *bromide*, $\text{C}_4\text{H}_8\text{OBr}_2\cdot\text{Hg}_2$, forming a fine, white, crystalline powder, and the *carbonate*, $\text{C}_4\text{H}_8\text{OHg}_2\cdot\text{CO}_3$, were also prepared.

A *polymeric ethenemercury iodide*, $(\text{C}_2\text{H}_3\text{IHg})_n$, separating from hot dilute alkali solution in fine spangles melting at 161° , and a *sulphide*, $(\text{C}_2\text{H}_3\text{Hg})_2\text{S}$, were also obtained.

T. H. P.

Action of Propylene and Butylene on Mercuric Salts. By JULIUS SAND and KARL A. HOFMANN (*Ber.*, 1900, 33, 1353—1358).—Although the action of ethylene on mercuric salts gives rise to four distinct classes of compounds (see preceding abstract), with propylene, only propanolmercury salts are obtained, whilst with isobutylene both butanolmercury salts and isobutylenemercury salts are formed.

Propanolmercury iodide, $\text{OH}\cdot\text{C}_3\text{H}_6\cdot\text{HgI}$, crystallises from ether in long, slender needles melting at 68° ; it is readily soluble in alcohol or ether. The *bromide*, when crystallised from a mixture of alcohol

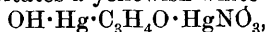
and ether, melts at 76° , and the *chloride* crystallises from ether in prisms melting at about 53° .

Butanolmercury bromide, $\text{OH}\cdot\text{C}_4\text{H}_8\cdot\text{HgBr}$, crystallises from benzene in small, shining prisms melting at 66° , and gives with ammonia a white *precipitate* of the composition $\text{OH}\cdot\text{C}_4\text{H}_8\cdot\text{HgBr}\cdot\text{NH}_3$; the *chloride* melts at 52° . On attempting to prepare the iodide, *butenemercury iodide*, $\text{C}_4\text{H}_7\text{IHg}$, is obtained which separates from benzene or carbon disulphide in beautiful, colourless prisms, and is soluble in ether.

From neutral mercuric sulphate solutions, *isobutylene* precipitates an intensely yellow powder of the composition $\text{C}_4(\text{OH})_6\text{Cl}_4\text{Hg}_4\cdot\text{H}_2\text{O}$.
T. H. P.

Action of Allyl Alcohol on Mercuric Salts. By JULIUS SAND and KARL A. HOFMANN (*Ber.*, 1900, 33, 1358—1364).—In acid solutions, the action of allyl alcohol on mercuric salts gives rise to allenemercury salts, $\text{XHg}\cdot\text{C}_3\text{H}_3$, which, in presence of alkali, take up water and pass into propenolmercury compounds, $\text{XHg}\cdot\text{C}_3\text{H}_4\cdot\text{OH}$.

Allenemercury nitrate, $\text{CH}_2\cdot\text{C}\cdot\text{CH}\cdot\text{HgNO}_3$, is almost insoluble in water or organic solvents, but dissolves readily in dilute aqueous caustic alkali; on heating, it explodes with a large flame. It is not decomposed by potassium cyanide, but is slowly attacked by boiling 10 per cent. hydrochloric acid. The corresponding *hydrogen sulphate*, $\text{CH}_2\cdot\text{C}\cdot\text{CH}\cdot\text{HgHSO}_4$, separates as a mass of colourless crystals from a mixture of allyl alcohol with a solution of mercuric sulphate in dilute sulphuric acid. A *double* compound of allenemercury chloride with mercuric chloride, $\text{HgCl}_2 + 2\text{C}_3\text{H}_3\cdot\text{HgCl}$, separates from a mixture of aqueous mercuric chloride and allyl alcohol as a white, flocculent precipitate. If allyl alcohol is left for some time in contact with mercuric nitrate solution, the addition of water to the filtrate from the allenemercury nitrate precipitates a yellowish-white *nitrate*,



which, with hydrochloric acid, yields calomel and an odour of acrylic acid.

Propenolmercury chloride, $\text{OH}\cdot\text{CH}_2\cdot\text{CH}\cdot\text{CH}\cdot\text{HgCl}$, forms a fine, white, crystalline precipitate, the *bromide* a heavy, white, crystalline powder, and the *iodide* fine spangles. *Propenolmercury cyanide*, $\text{OH}\cdot\text{CH}_2\cdot\text{CH}\cdot\text{CH}\cdot\text{HgCN}$, forming a thick, white precipitate, the *sulphide*, and a *basic carbonate* were also prepared. Most of these salts are soluble in ammonia solution, and all dissolve in a solution of potassium hydroxide containing 1 mol. of the base for every atom of mercury present. They cannot be separated into their components by hydrochloric acid, as the strength of acid necessary decomposes allyl alcohol. The salts are oxidised by permanganate, but oxalic acid is the only product identified.
T. H. P.

Action of Cyanogen Bromide and Aluminium Chloride on Benzenoid Hydrocarbons and Phenol Ethers. By ROLAND SCHOLL and WILHELM NÖRR (*Ber.*, 1900, 33, 1052—1058).—When cyanogen bromide acts on benzenoid hydrocarbons in presence of aluminium chloride, the principal products are cyanidins, whilst the

simple nitriles and brominated hydrocarbons are formed only in small quantities. In the case of anisole, however, the product consists for the most part of anisonitrile and *p*-bromoanisole (compare Friedel and Crafts, *Ann. Chim. Phys.*, 1884, [vi], 1, 528).

In these reactions, it is always the hydrogen in the para-position to a group already present which suffers replacement, and in the case of *p*-xylene and *p*-cymene, in which this is impossible, action does not occur.

Benzene and cyanogen bromide react in presence of aluminium chloride at 50°, yielding considerable quantities of cyaphenin. As the latter substance is not formed by the action of aluminium chloride on benzonitrile, it follows that it results from the action of benzene on the cyanuric bromide which is formed in the first instance.

Cyan-o-xylol, $C_{27}H_{27}N_3$ ($Me_2:C=1:2:4$) is formed from *o*-xylene. It crystallises from benzene in small needles which sinter at 204° and melt and partially decompose at 210°. It yields *p*-xylic acid when heated at 220° with hydrochloric acid. *Cyan-m-xylol*, $C_{27}H_{27}N_3$ [$Me_2:CN=1:3:4$], from *m*-xylene, crystallises from hot acetone in colourless leaflets melting at 154–155°. A. L.

Law Governing the Elimination of Halogens from the Benzene Ring. By AUGUST KLAGES and C. LIECKE (*J. pr. Chem.*, 1900, [ii], 61, 307–329).—A long series of experiments show that the presence of an alkyl group in the ortho- or para-position in the benzene ring has an equal effect on the elimination of a halogen, whilst one in the meta-position has much less influence, and that two alkyl groups in the diortho-positions or the orthopara-positions have a much greater influence than in the dimeta-positions. Alkyl groups, therefore, exercise an influence on chemical reactions, not only in the ortho- and diortho-positions, but also in the orthopara-positions. The introduction and elimination of a halogen group is more easily effected from homologues of benzene than from benzene itself. A similar law holds good for hydroxy-compounds; for example, *o*- and *p*-iodophenols are much more easily converted by hydrogen iodide into phenol than *m*-iodophenol.

The following new compounds are described: *m*-chloriodobenzene, which boils at 230°; 3-iodo-*o*-xylene, which is a colourless oil boiling at 125–126° under 15 mm. pressure; 2-iodo-*m*-xylene, which is an oil boiling at 228–230°, and volatile with steam; 2-iodo-*p*-xylene, which boils at 229°. R. H. P.

Formation of Tri-substituted from Di-substituted Benzene Derivatives. By ARNOLD F. HOLLEMAN (*Proc. K. Akad. Wetensch., Amsterdam*, 1900, 2, 478–480).—Benzoic acid, when nitrated at 0°, yields the three mononitro-compounds in the following proportions: 18.5, 80.2, and 1.3 per cent. for the ortho-, meta-, and para-isomerides respectively (Abstr., 1899, i, 759). The three dinitrobenzenes are all produced by the direct nitration of nitrobenzene at 0°, the relative amounts of the ortho-, meta-, and para-derivatives being respectively 6.4, 93.5, and 0.1 per cent.

In the nitration of the three nitrobenzoic acids, the entering radicle

f f 2

is subjected to the joint influence of the two groups already present in the molecule. For example, in *o*-nitrobenzoic acid, the positions 3, 4, 5, and 6 are still unoccupied, and considering each of these in turn, it is seen that if the carboxyl group alone were present, 80.2 per cent. of the product would contain the entering group in position 3, whereas only 6.4 per cent. of the whole would have this orientation if the influence of the nitro-group alone is taken into account; the product of these two percentages, $504 (= 6.4 \times 80.2)$, is taken as the numerical expression of the tendency to form the 2:3-dinitrobenzoic acid, the corresponding factors for the 2:4-, 2:5-, and 2:6-isomerides being 100, 8, and 1730 respectively. It is found that the 2:6-dinitrobenzoic acid, which corresponds with the highest factor, is the chief product of nitration. In *m*-nitrobenzoic acid, the coefficients for the unoccupied positions 2, 4, 5, and 6 are 118, 8, 7499, and 1.8 respectively; experiment shows that the 3:5-dinitrobenzoic acid, corresponding with the highest factor, is the sole product.

When *p*-nitrobenzoic acid is nitrated, the entering radicle may take up one or other of two positions; the factor for position 2 is 1730, whilst that for position 3 is 504; the mixture of dinitro-compounds actually produced consists mainly of the 2:4-compound, together with a small amount of the 3:4-isomeride.

A similar process of reasoning was adopted in predicting the constitution of the chloronitrobenzoic acids obtained by nitrating the three chlorobenzoic acids; these theoretical deductions are confirmed by Montagne's experiments (*Dissertation Leiden*, 1899). On nitrating *o*-chlorobenzoic acid, the main product is the 2-chloro-5-nitrobenzoic acid, accompanied by traces of the 2:3-acid; *m*-chlorobenzoic acid yields the 3:6-acid, together with small quantities of its isomerides, whilst *p*-chlorobenzoic acid gives rise to the 4:3-acid only.

G. T. M.

m-Xylylamine and *m*-Methylphenylethylamine. By F. SOMMER (*Ber.*, 1900, 33, 1073—1081).—The crude *m*-methylbenzylamine, obtained by reducing *m*-toluonitrile with alcohol and sodium, is easily purified by conversion into the corresponding carbamide, $C_8H_9 \cdot NH \cdot CO \cdot NH_2$, which crystallises in slender, white needles melting at 148°. The base regenerated from the latter is identical in all its properties with Brömme's *m*-xylylamine (*Abstr.*, 1888, 1295). The xylylamine prepared by Pieper from xylyl chloride (*Annalen*, 1869, 151, 129) was an impure form of the same substance.

The following new derivatives of the base have been prepared. The *hydrochloride*, colourless crystals melting at 208°; the *sulphate*, white leaflets melting and decomposing at 248°; the *mercurichloride*, $(C_8H_9 \cdot NH_2 \cdot HCl)_2 \cdot HgCl_2$, white leaflets melting at 184°.

The *m*-xylyl alcohol prepared from the base is identical with the substance obtained by Radziszewski and Wispek from ethyl *m*-xylyl-acetoacetate (*Abstr.*, 1882, 1283), and the corresponding aldehyde with that obtained from *m*-xylene by the Étard reaction. *m*-Xylylaldehyde-semicarbazone, $C_8H_8 \cdot N \cdot NH \cdot CO \cdot NH_2$, crystallises from dilute alcohol in slender needles, and melts at 216°.

m-Methylphenylethylamine, $C_6H_4Me \cdot CH_2 \cdot CH_2 \cdot NH_2$, formed by re-

ducing *m*-xylyl cyanide with alcohol and sodium, is a colourless liquid, has powerful basic properties, and boils at 214—215° under 744 mm. pressure. The *hydrochloride* melts at 159°, and the *platinichloride*, $(C_9H_{13}N)_2 \cdot H_2PtCl_6$, is amorphous, and melts and decomposes at 243°. The *aurichloride* forms large, golden leaflets, which sinter at 73° and melt indefinitely at 85°. The *picrate* crystallises in beautiful, yellow leaflets and melts at 173°. The *carbamide*, $C_9H_{11} \cdot NH \cdot CO \cdot NH_2$, forms white leaflets and melts at 84°. The *benzoyl* derivative, $C_9H_{11} \cdot NHBz$, was obtained as a crystalline mass.

2-*m*-Methylphenylethyldihydroisoinsole, $C_6H_4 \langle \begin{smallmatrix} CH_2 \\ CH_2 \end{smallmatrix} \rangle N \cdot C_9H_{11}$, is formed when *o*-xylylene dibromide is heated with *m*-methylphenylethylamine. The *platinichloride*, $(C_{17}H_{19}N)_2 \cdot H_2PtCl_6$, forms small, yellow crystals, which melt and decompose at 216°. A. L.

Hydroxyethylideneoxanilide. By HANS VON PECHMANN and OTTO ANSEL (*Ber.*, 1900, 33, 1297—1301. Compare *Abstr.*, 1898, i, 135, and this vol., i, 287).—The final product of the action of acetic anhydride on glyoxime-N-phenyl ether is vinylideneoxanilide. By allowing the acetic anhydride to act for only 3 minutes, the authors have isolated an intermediate product, *hydroxyethylideneoxanilide*, which crystallises in lustrous, white leaflets melting at 174°, gives a yellow coloration with concentrated sulphuric acid, is only with difficulty attacked by oxidising agents, and on further treatment with acetic anhydride and anhydrous sodium acetate, yields vinylideneoxanilide. On treatment with an ethereal solution of diazomethane, it yields *methoxyethylideneoxanilide*, which crystallises in soft, white, matted needles melting at 223—224°, and on hydrolysis yields oxanilide.

In an analogous manner, glyoxime-N-phenyl ether and propionic anhydride yield *hydroxypropylideneoxanilide*, which melts at 160°, gives a yellow coloration with sulphuric acid, and is easily converted into methylvinylideneoxanilide. R. H. P.

Sulphonic Acids of the Acetylxylylides. By ALFRED JUNGHAHN (*Ber.*, 1900, 33, 1364—1366).—The sulphonic acids of the acetylxylylides can be obtained in the solid form by direct sulphonation, and the corresponding acids of the acetyltoluidines and of acetylaniline can be prepared in a similar manner. *Acetyl-1 : 4 : 2-xylylidene-5-sulphonic acid* crystallises with $2H_2O$ in long, greyish-white needles; on hydrolysis, it yields 1 : 4 : 2-xylylidene-5-sulphonic acid. *Acetyl-1 : 3 : 4-xylylidene-6-sulphonic acid* crystallises with $2H_2O$ in small, white, quadratic prisms or large tablets. The sulphonic acids of acetyltoluidine and acetylaniline will form the subject of a future communication.

A. H.

Phenylcyanamide. By WILHELM TRAUBE and ERNST VON WEDELSTÄDT (*Ber.*, 1900, 33, 1383—1386. Compare this vol., i, 340).—Phenylmethylcyanamide is readily obtained when phenylcyanamide is treated with sodium ethoxide and methyl iodide. *Phenylbenzylcyanamide* melts at 64°, is insoluble in water, but dissolves readily in

most organic solvents, and, when boiled with dilute hydrochloric acid, yields benzylaniline.

When a considerable excess of ethylene bromide is added to an alcoholic solution of sodium phenylcyanamide, the product is *phenylbromoethylcyanamide*, $\text{CN}\cdot\text{NPh}\cdot\text{CH}_2\cdot\text{CH}_2\text{Br}$, which, after recrystallisation from dilute alcohol, melts at 42° ; when, however, an excess of the sodium derivative is used, *dicyanodiphenylethylenediamine*, $\text{C}_2\text{H}_4(\text{NPh}\cdot\text{CN})_2$, is formed; this melts at 133° , and when boiled with hydrochloric acid is decomposed, yielding a substance which, on the addition of sodium hydroxide, separates in the form of colourless crystals melting at 162° .

Ethyl cyanophenylaminoacetate, $\text{CN}\cdot\text{NPh}\cdot\text{CH}_2\cdot\text{CO}_2\text{Et}$, melts at 49° ; chloroacetone and sodium phenylcyanamide give a compound melting at 130° .
J. J. S.

Action of Certain Acid Reagents on Substituted Carbamides. By FRANK B. DAINS (*J. Amer. Chem. Soc.*, 1900, 22, 181—198).—By the action of acid chlorides and anhydrides on substituted carbamides, acylcarbamides are probably formed, but, on account of the high temperature required to effect reaction, only their decomposition products can be isolated.

Cain and Cohen (*Trans.*, 1891, 59, 329) have shown that when pure acetic acid and diphenylthiocarbamide are heated at 130° — 140° for 3—4 hours, diphenylcarbamide is produced. The author finds that if this mixture is heated on the water-bath for 30 hours, it yields phenylthiocarbimide, acetanilide, and triphenylguanidine, but that if aqueous acetic acid (75 per cent.) is employed, the final products are acetylaniline and diphenylcarbamide. Triphenylguanidine picrate melts at 180° , and not at 178° , as usually stated. When butyric acid is allowed to act on diphenylthiocarbamide at 140° — 160° , carbon dioxide and hydrogen sulphide are evolved, and butyrylaniline and diphenylcarbamide obtained. Benzoic acid and salicylic acid react with diphenylthiocarbamide, and benzoic acid with di-*p*-tolylthiocarbamide, in a corresponding manner.

When diphenylthiocarbamide is heated with oxalic acid at 160° — 180° , the products are carbon dioxide, hydrogen sulphide, and oxanilide. Succinic acid reacts with diphenylthiocarbamide at 170° with formation of carbon dioxide, hydrogen sulphide, succinyl, and succinylaniline, together with small quantities of aniline and phenylthiocarbimide; a similar decomposition occurs when succinic anhydride is employed, as shown by Dunlap (*Abstr.*, 1896, i, 471). The action of phthalic acid on diphenylthiocarbamide results in the production of hydrogen sulphide, carbon dioxide, phenylthiocarbimide, phthalanil, and a little aniline; phthalic anhydride behaves in a similar manner, as pointed out by Dunlap (*loc. cit.*). When di-*p*-tolylthiocarbamide is heated with phthalic anhydride at 160° , carbon oxysulphide, *p*-tolylthiocarbimide, and *p*-tolylphthalanil are produced.

The acyl derivative, formed by the interaction of an acid chloride and a disubstituted carbamide, appears to break down into an anilide and a carbimide, which further react, giving carbon dioxide and an amidine derivative. When diphenylcarbamide and acetyl chloride are

heated together for 3 hours at 150° , carbon dioxide, acetylaniline, and α -diphenylethenylamidine are produced; the platinichloride of the last-mentioned substance melts at 210° , and the picrate at 165° . *α -Diphenylbutenylamidine*, $C_5H_7 \cdot C(NPh) \cdot NHPh$, obtained, together with carbon dioxide and butyrylaniline, by the action of butyryl chloride on diphenylcarbamide at 150 – 170° , crystallises from alcohol in needles, melts at 105° , and yields a platinichloride. A similar reaction takes place when benzoyl chloride is employed; diphenylbenzamidine picrate melts at 216° .

Deninger (Abstr., 1895, i, 461) has shown that, in the presence of pyridine, acid chlorides react with diphenylthiocarbamide at the ordinary temperature with formation of stable substitution products. The author finds that, in the absence of pyridine, heat is required to effect reaction, and no acyl thiocarbamide can be isolated, but a thiocarbimide and an anilide are the principal products, whilst occasionally a small quantity of an amidine base is formed. The action of acetyl, butyryl, and benzoyl chlorides on diphenylthiocarbamide, and the action of benzoyl chloride on di-*m*-xylylthiocarbamide and on di-*o*-tolylthiocarbamide are described. Acetyl chloride reacts with allylphenylthiocarbamide, giving rise to phenylthiocarbimide and *N*-phenylpropylene- μ -thiocarbamide.

The isocarbamide ethers are readily attacked by organic acids, as the author has previously pointed out (Abstr., 1899, i, 592), whereas the thio-ethers are remarkably stable towards them. By the action of acetic anhydride on amylsodi-*o*-tolylcarbamide at 150 – 160° , amyl acetate, *o*-acetyltoluidine, and a trace of *o*-ditolylcarbamide are formed; under similar conditions, ethylsodiphenylcarbamide yields ethyl acetate and acetylaniline, while methylsodi-*o*-tolylcarbamide furnishes methyl acetate and *o*-acetyltoluidine.

When ethylsodiphenylthiocarbamide is boiled with acetic anhydride, an acetyl additive *product*, $NHPh \cdot C(NPhAc)(SEt) \cdot OAc$, is obtained as a yellow oil, which is soluble in ether, and is decomposed by alcoholic potassium hydroxide with formation of mercaptan and diphenylcarbamide; if, however, the mixture is heated in a sealed tube at 190° , mercaptan, ethyl acetate, and acetylaniline are produced. *Acetylethylsodiphenylthiocarbamide*, $NPh \cdot C(NPhAc) \cdot SEt$, is obtained as a thick oil by the action of acetyl chloride (1 mol.) on a chloroform solution of ethylsodiphenylthiocarbamide (2 mols.) at the ordinary temperature; it is not affected by boiling with glacial acetic acid, but on heating with alcoholic sodium hydroxide, yields sodium acetate, mercaptan, and diphenylthiocarbamide. Benzoyl chloride reacts with ethylsodiphenylthiocarbamide in a similar manner, yielding an oily *benzoyl* derivative, which is decomposed on heating. E. G.

Colour of Picric Acid and its Solutions. By WILHELM MARCKWALD (Ber., 1900, 33, 1128).—Picric acid, when crystallised from concentrated hydrochloric acid, is nearly colourless, but on washing the colourless crystals with water the yellow colour is restored; moreover, the acid mother liquor, which is initially nearly colourless, becomes yellow on strongly diluting. The colour of picric acid thus appears to be due to the coloured ion, $C_6H_2(NO_2)_3O$; when pure

yellow picric acid is dried in a vacuum over sulphuric acid, it becomes colourless owing to the prevention of dissociation within the crystals. A solution of picric acid in light petroleum is nearly colourless, but becomes bright yellow on shaking with water. W. A. D.

Action of Ethylidene Chloride on Phenols. By R. FOSSE and J. ETLINGER (*Compt. rend.*, 1900, 130, 1194—1196).—*Acetal m-cresol*, $\text{CH}_3 \cdot \text{CH}(\text{OC}_6\text{H}_4\text{Me})_2$, obtained by heating together 1 mol. of ethylidene chloride, 2 mols. of potassium hydroxide, and 2 mols. of *o*-cresol at 120° in a sealed tube, is a colourless, oily liquid boiling at 180 — 185° under 27 mm. pressure, and at 173 — 175° under 16 mm. pressure, is insoluble in water or alkalis, but soluble in alcohol, ether, or benzene. When cooled to a low temperature, it solidifies to a white mass which melts at about 12° . When hydrolysed with dilute sulphuric acid, it yields acetaldehyde and *o*-cresol.

Acetal p-cresol is a colourless, oily liquid boiling at 200 — 204° under 22 mm. pressure, which can be solidified to a white mass melting at 15 — 17° ; in other respects, it resembles the ortho-compound. When resorcinol, potassium hydroxide, and ethylidene chloride are heated together in a sealed tube, the compound produced is identical with the acetal resorcinol obtained by Causse from acetaldehyde and resorcinol (*Abstr.*, 1887, 40). H. R. LE S.

2:6-Diphenyl-4-nitrophenol and 2-Phenyl-4-nitrophenol. By HENRY B. HILL (*Ber.*, 1900, 33, 1241—1242).—*2:6-Diphenyl-4-nitrophenol*, obtained by the condensation of dibenzyl ketone with nitromalonic aldehyde in alkaline solution (compare Hill and Torrey, *Abstr.*, 1899, i, 788), crystallises from alcohol in colourless prisms and melts at 135 — 136° (corr.); the corresponding aminophenol, quinone, and quinol, melt respectively at 149 — 150° (corr.), 135 — 136° (corr.), and 179 — 180° (corr.) (compare Borsche, this vol., i, 24).

2-Phenyl-4-nitrophenol, obtained similarly from benzyl methyl ketone, crystallises from boiling water or dilute acetic acid in long, yellow needles, and melts at 125 — 126° ; the corresponding aminophenol melts at 198 — 199° (corr.), and the quinone at 112 — 113° (corr.) (compare Borsche, *loc. cit.*). W. A. D.

Preparation of Anthranilic Acid from *o*-Nitrotoluene. By L. PREUSS and A. BINZ (*Zeit. angew. Chem.*, 1900, 16, 385—386).—Anthranilic acid can be prepared in small yield by fusing *o*-nitrotoluene with powdered sodium or potassium hydroxide. It is readily formed when *o*-nitrotoluene is heated for some hours on the water-bath with concentrated solutions of the alkalis, but dilute solutions produce only a trace. Alcoholic potash is also effective, so that anthranilic acid is produced when *o*- and *p*-nitrotoluenes are separated by Reverdin and La Harpe's method (*Bull. Soc. Chim.*, 1880, [ii], 50, 44). Atmospheric oxygen plays no part in the reaction. R. L. J.

Formation of Chains. XLIV. The Three Sodium Tolyloxides and Ethyl Esters of α -Bromo-fatty Acids. By CARL A. BISCHOFF (*Ber.*, 1900, 33, 1249—1261).—*Ethyl α -o-tolyloxypropionate*, $\text{C}_7\text{H}_7 \cdot \text{O} \cdot \text{CHMe} \cdot \text{CO}_2\text{Et}$, is a colourless oil of sp. gr. 1.043 at $19^\circ/19^\circ$; which boils at 140° under 10 mm., and at 245 — 246° under 760 mm.

pressure ; it is readily hydrolysed by aqueous potassium hydroxide to the *o*-acid, which separates from ether in large crystals, and melts at 93°. The *m*-ester is a colourless oil which boils at 252° under 743 mm. pressure ; the *m*-acid crystallises from a mixture of ether and petroleum in plates and needles, and from benzene in slender needles, dissolves readily in other solvents, melts at 106—108°, and gives a violet coloration when warmed with nitric acid, a property which is also shared by the other *m*-tolylxy-acids. The *p*-ester is a colourless oil of density 1·043 at 19°/4°, which boils at 150—151° under 33 mm. pressure, and at 255—256° under 760 mm. pressure ; the *acid* crystallises in long, glistening needles, and melts at 100—101°.

Ethyl α-o-tolylxybutyrate, $C_7H_7 \cdot O \cdot CH_2Et \cdot CO_2Et$, is a colourless oil which boils at 254—255° ; the *o*-acid crystallises from light petroleum in colourless needles, dissolves readily in organic solvents, but only slightly in water, and melts at 49—52°. The *m*-ester is a colourless oil which boils at 262—263° under 745 mm. pressure ; the *m*-acid crystallises from light petroleum in needles and melts at 72—74°. The *p*-ester boils at 266·5° under 743 mm. pressure ; the *acid* crystallises from light petroleum in needles and four-sided tablets, and melts at 63—65°.

Ethyl α-o-tolylxyisobutyrate is a colourless oil of sp. gr. 1·032 at 19°, which boils at 147° under 39 mm., and at 245—248° under 760 mm. pressure ; the *acid* crystallises in stout, rectangular prisms, and melts at 75—76°. The *m*-ester is a colourless oil, and boils at 253° under 745 mm pressure ; the *m*-acid crystallises from light petroleum in square tablets, and melts at 66·5—67·5°. The *p*-ester is a colourless oil of sp. gr. 1·032 at 19°, boils at 150° under 39 mm. pressure, and at 254—258° under 760 mm. pressure ; the *p*-acid crystallises from light petroleum in large six- and eight-sided tablets, and melts at 71—72°.

Ethyl o-tolylxyisovalerate, $C_7H_7 \cdot O \cdot CHPr^i \cdot CO_2Et$, is a colourless oil which boils at 258—261° ; the *acid* crystallises from light petroleum in soft, slender needles, and melts at 86—87°. The *m*-ester is a colourless oil which boils at 265—266° under 745 mm. pressure ; the *m*-acid crystallises from light petroleum in colourless prisms, and melts at 61—63·5°. The *p*-ester boils at 145—148° under 55 mm. pressure, and at 265—271° under 760 mm. pressure ; the *p*-acid crystallises from light petroleum in colourless, four-sided tablets, and melts at 81—82°.

T. M. L.

Formation of Chains. XLV. Sodium Xylyloxides and Ethyl Esters of α-Bromo-fatty Acids. By CARL A. BISCHOFF (*Ber.*, 1900, 1261—1269).—*Ethyl α-o-xylyloxypropionate*,

$C_6H_3Me_2 \cdot O \cdot CHMe \cdot CO_2Et$ [Me : Me : OR = 1 : 2 : 4], is a yellowish oil which boils at 268—273° under 773 mm. pressure ; the *o*-acid crystallises from a mixture of ether and light petroleum in square rods and plates, and melts at 85—88°. The *m*-ester [Me : Me : OR = 1 : 3 : 4] boils at 264·5° under 771 mm. pressure ; the *m*-acid crystallises from a mixture of ether and light petroleum in colourless prisms, and melts at 82—87·5°. The *p*-ester [Me : Me : OR = 1 : 4 : 5] is a colourless oil which boils at 259° under 782 mm. pressure ; the *p*-acid crystallises from light petroleum in four-sided prisms and tablets, and melts at 105—106·5°.

Ethyl α-o-xylyloxybutyrate is a yellowish oil and boils at 275—280° under 773 mm. pressure. The *o-acid* crystallises from light petroleum in colourless needles, and melts at 73—76°. The *m-ester* is a colourless oil which boils at 267—271° under 769 mm. pressure. The *m-acid* crystallises from a mixture of ether and light petroleum in soft, colourless needles, and melts at 64·3—65·3°. The *p-ester* boils at 265—266° under 765 mm. pressure. The *p-acid* crystallises from a mixture of ether and light petroleum in soft, colourless needles, and melts at 87—90°.

Ethyl α-o-xylyloxyisobutyrate is a yellowish oil of characteristic odour, and boils at 263—268° under 774 mm. pressure; the *acid* crystallises from light petroleum in yellowish plates, and melts at 86—90·5°. The *m-ester* boils at 255—258° under 769 mm. pressure. The *m-acid* was obtained as a yellow oil. The *p-ester* is a colourless oil which boils at 265—266° under 767 mm. pressure. The *p-acid* crystallises from a mixture of ether and light petroleum in four-sided tablets and melts at 114°.

Ethyl α-o-xylyloxyisovalerate is a colourless oil which boils at 275—283° under 744 mm. pressure. The *o-acid* crystallises from light petroleum in prisms, and melts at 49·5—52°. The *m-ester* is a colourless oil which boils at 267—274° under 769 mm. pressure; the *m-acid* is a yellowish oil which boils at 213° under 42 mm. pressure. The *p-ester* is a colourless oil which boils at 270° under 769 mm. pressure. On hydrolysis, it gives crystals of *p*-xylenol in addition to the *p-acid* which was obtained as a yellow oil. T. M. L.

Formation of Chains. XLVI. Sodium Derivatives of Carvacrol, Thymol, and ψ -Cumenol with Ethyl Esters of α -Bromofatty Acids. By CARL A. BISCHOFF (*Ber.*, 1900, 33, 1269—1277).—*Ethyl α-carvacroxypropionate*, $C_6H_3MePr \cdot O \cdot CHMe \cdot CO_2Et$ [$Me : Pr : OR = 1 : 4 : 6$], is a colourless oil which boils at 277—279° under 751 mm. pressure; the *acid* separates from light petroleum in colourless crystals and melts at 81·5—82·5°.

Ethyl α-carvacroxybutyrate boils at 283—286° under 751 mm. pressure; the *acid* boils at 224—225° under 59 mm. pressure, and solidifies to crystals which melt at 42·5—43·5°.

Ethyl α-carvacroxyisobutyrate boils at 262—272° under 751 mm. pressure, the *acid* at 190—200° under 93 mm. pressure.

Ethyl α-carvacroxyisovalerate boils at 280—292° under 762 mm. pressure, the *acid* at 226—229° under 68 mm. pressure.

Ethyl α-thymoxypropionate [$Me : Pr : OR = 1 : 4 : 5$] boils at 267—272° under 760 mm. pressure; the *acid* crystallises from a mixture of ether and light petroleum in large, colourless tablets, and melts at 68·5—69°.

Ethyl α-thymoxybutyrate boils at 273—278° under 773 mm. pressure; the *acid* crystallises from a mixture of ether and light petroleum in large, triclinic prisms, and melts at 74—76·5°.

Ethyl α-thymoxyisobutyrate boils at 258—263° under 760 mm. pressure; the *acid* crystallises from light petroleum in minute needles and melts at 69—71°.

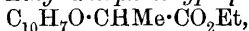
Ethyl α-thymoxyvalerate boils at 275—283° under 760 mm. pressure, and the *acid* boils at 228—229° under 60 mm. pressure.

Ethyl α -cumenoxypropionate,

$C_6H_5Me_3O \cdot CHMe \cdot CO_2Et$ [Me : Me : OH : Me = 1 : 2 : 4 : 5],
boils at 147—149° under 20 mm. pressure; the *acid* crystallises from alcohol in colourless tablets and melts at 147°. T. M. L.

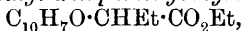
Formation of Chains. XLVII. Sodium Naphthyloxides and Ethyl Esters of α -Bromo-fatty Acids. By CARL A. BISCHOFF (*Ber.*, 1900, 33, 1386—1392).—The sodium derivatives of α - and β -naphthol (compare Schäffer, *Annalen*, 1869, 152, 286) may readily be obtained in a pure state by treating the naphthols with the theoretical amount of sodium ethoxide dissolved in alcohol and subsequent heating under reduced pressure until the weight is constant. These sodium derivatives have been respectively heated for 4 hours at 160° with the ethyl esters of α -bromopropionic, α -bromobutyric, α -bromoisobutyric, and α -bromoisovaleric acids, and the resulting products fractionated first under ordinary and, finally, under reduced pressure.

[With KISLIANSKY.]—*Ethyl α -naphthoxypropionate*,



is a pale yellow oil, distilling at 195° under 8 mm., or at 205° under 22 mm. pressure. The *acid* crystallises from benzene in minute, colourless plates melting at 153°, and is only sparingly soluble in hot water, cold benzene, or light petroleum.

[With LIPSCHITZ.]—*Ethyl α -naphthoxybutyrate*,



distils at 190—194° under 5 mm. pressure, and has a specific gravity 1.102 at 18.6°/4°. The *acid* crystallises in colourless needles and melts at 113—114°. *Ethyl α -naphthoxyisobutyrate*, $C_{10}H_7O \cdot CMe_2 \cdot CO_2Et$, distils at 190—193° under 6 mm. pressure, and the *acid* melts at 130—131°. *Ethyl α -naphthoxyisovalerate* distils at 208° under 10 mm. pressure, and the corresponding *acid* melts at 89.5—90.5°.

[With SLOBODSKOI.]—*Ethyl β -naphthoxypropionate* crystallises from alcohol in rhombic prisms. The *acid* crystallises in mono- or tri-clinic plates melting at 107—108°.

[With CON.]—*Ethyl β -naphthoxybutyrate* is a pale yellow oil distilling at 200—203° under 12 mm. pressure. The *acid* crystallises from water in needles melting at 126.5°.

[With SIW.]—*Ethyl β -naphthoxyisobutyrate* distils at 195—200° under 6 mm. pressure, and the *acid* crystallises in prismatic plates melting at 123°.

[With DOWGALLO.]—*Ethyl β -naphthoxyisovalerate* boils at 212° under 13 mm. pressure, and the *acid* crystallises in needles melting at 140°.

Quantitative experiments have been made by boiling the two sodium derivatives (1 mol.) with solutions of the bromo-esters (2 mols.) in light petroleum (b. p. 65—70°) for 1 hour. The following results show the percentage of the sodium derivative that has entered into reaction :

	α -Naphthol.		β -Naphthol.	
α -Bromopropionate	81.0	82.5	91.0	91.5
α -Bromobutyrate	84.5	85.0	84.0	88.0
α -Bromoisobutyrate	15.0	20.5	37.0	39.0
α -Bromoisovalerate	11.0	9.5	21.0	21.5

J. J. S.

Formation of Chains. XLVIII. Guaiacol Derivatives. By CARL A. BISCHOFF (*Ber.*, 1900, **33**, 1392—1397).—The sodium derivative of guaiacol is readily obtained by treating guaiacol with an alcoholic solution of sodium ethoxide and heating the residue to 120° under reduced pressure. This sodium derivative has been treated with the ethyl esters of the α -bromo-fatty acids mentioned in the preceding abstract.

Ethyl α -guaiacoxypionate, $\text{OMe}\cdot\text{C}_6\text{H}_4\cdot\text{O}\cdot\text{CHMe}\cdot\text{CO}_2\text{Et}$, is a colourless liquid with a strong, alliaceous odour, and distils at 272—277° under 740 mm. pressure. The *acid* melts at 85° and dissolves in most organic solvents; with hydrochloric acid, it gives a reddish-yellow colour, and with warm nitric acid a bordeaux red. When the acid is heated with phenetidine for 8 hours at 160°, it yields *guaiacoxypionylphenetidine*, $\text{OMe}\cdot\text{C}_6\text{H}_4\cdot\text{CHMe}\cdot\text{CO}\cdot\text{NH}\cdot\text{C}_6\text{H}_4\cdot\text{OEt}$, which crystallises from alcohol in colourless needles melting at 96.5°. It is non-poisonous, and may be employed in cases of influenza. The same compound may be more readily prepared by the action of the sodium derivative of guaiacol on an alcoholic solution of α -bromopropionylphenetidine (melting at 135°). Bromoacetylphenetidine melts at 171.5—176°, and reacts with an alcoholic solution of sodium guaiacol, yielding Lederer's guaiacoxylacetylphenetidine, melting at 103°.

Ethyl α -guaiacoxybutyrate, $\text{OMe}\cdot\text{C}_6\text{H}_4\cdot\text{O}\cdot\text{CHEt}\cdot\text{CO}_2\text{Et}$, distils at 274—276° under 744 mm. pressure, and has an odour similar to that of butyric acid. The *acid* crystallises in needles melting at 75—76°. *Ethyl α -guaiacoxisobutyrate*, $\text{OMe}\cdot\text{C}_6\text{H}_4\cdot\text{O}\cdot\text{CMe}_2\cdot\text{CO}_2\text{Et}$, distils at 272—273° under atmospheric pressure, and the *acid* is an oil. *Ethyl α -guaiacoxisovalerate* distils at 275—285° at 751 mm. pressure, and yields an *acid* melting at 98—98.5°.

Ethyl guaiacoxymalonate, $\text{OMe}\cdot\text{C}_6\text{H}_4\cdot\text{O}\cdot\text{CH}(\text{CO}_2\text{Et})_2$, distils at 205° under 13 mm. pressure, and when hydrolysed yields the corresponding acid, which reacts with phenetidine.

The following numbers give the percentage of the sodium derivative which enters into reaction when heated in light petroleum (b. p. 65—70°) solution for 1 hour with the different esters:

Ethyl α -bromopropionate	39.5	40.0
Ethyl α -bromobutyrate	28.0	28.5
Ethyl α -bromoisobutyrate	3.2	3.5
Ethyl α -bromisovalerate	2.5	3.5

From these results, it appears that guaiacol lends itself less readily to chain formation than any of the phenols hitherto investigated.

J. J. S.

Formation of Chains. XLIX. Derivatives of the three Ethyl Hydroxybenzoates. By CARL A. BISCHOFF [with, in part, BELAKOWSKI, GUNTUM, KOCH, KRUSENSTIERN, MERGENTHALER, RONTAL, and RZUCHOWSKI] (*Ber.*, 1900, **33**, 1398—1407. Compare Rossing, *Abstr.*, 1885, 388; Auwers and Haymann, *ibid.*, 1895, i, 44).—The sodium derivatives of ethyl *o*-, *m*-, and *p*-hydroxybenzoates (1 mol.) have been heated with the ethyl esters of α -bromo-fatty acids (2 mols.) for 4 hours at 160° and the products investigated.

Ethyl α-salicyloxypropionate, $\text{CO}_2\text{Et} \cdot \text{C}_6\text{H}_4 \cdot \text{O} \cdot \text{CHMe} \cdot \text{CO}_2\text{Et}$, distils at $214\text{--}215^\circ$ under 55 mm. pressure, and on hydrolysis yields the corresponding *acid* melting at $137\text{--}139^\circ$. The bye-products which are formed in the preparation of the ester have not been obtained in a pure state.

Ethyl α-salicyloxybutyrate distils at $199\text{--}201^\circ$ under 17 mm. pressure, and the *acid* crystallises in colourless plates melting at 130° . *Ethyl α-salicyloxyisobutyrate* distils at 193° under 21 mm. pressure, and the corresponding *acid* crystallises in needles melting at $108\text{--}109^\circ$. *Ethyl salicyloxyisovalerate* distils at $185\text{--}190^\circ$ under 4 mm. pressure, and the corresponding *acid* melts at $129\text{--}130^\circ$. In the preparation of the ester, a considerable amount of *ethyl isopropylketocoumarancarboxylate*, $\text{C}_6\text{H}_4 \begin{array}{c} \text{CO} \\ \diagup \quad \diagdown \\ \text{O} \end{array} \text{CPr}^s \cdot \text{CO}_2\text{Et}$, is always formed; it crystallises in long, colourless needles melting at $77\text{--}78^\circ$.

The following numbers give the percentage amounts of the sodium derivatives entering into reaction when boiled with the ethyl esters (2 mols.) for 1 hour in light petroleum (b. p. $65\text{--}70^\circ$):

	<i>Ortho.</i>		<i>Meta.</i>		<i>Para.</i>	
Ethyl α-bromopropionate...	21.55	23.05	28.0	29.8	13.25	16.0
„ α-bromobutyrate ...	8.25	9.1	12.0	13.3	11.75	12.5
„ α-bromoisobutyrate...	1.8	2.5	2.55	2.9	1.5	3.54
„ α-bromoisovalerate...	0.6	0.6	2.85	3.14	2.0	3.0

It thus appears that sodium derivatives of the ester of hydroxybenzoic acids condense less readily even than the sodium derivative of guaiacol.

Ethyl hydrogen p-carboxyphenoxypropionate,

$\text{CO}_2\text{H} \cdot \text{C}_6\text{H}_4 \cdot \text{O} \cdot \text{CHMe} \cdot \text{CO}_2\text{Et}$ or $\text{CO}_2\text{Et} \cdot \text{C}_6\text{H}_4 \cdot \text{O} \cdot \text{CHMe} \cdot \text{CO}_2\text{H}$, crystallises in colourless needles melting at 103° ; the normal *ethyl ester* is a thick, colourless oil distilling at $210\text{--}215^\circ$ under 20 mm. pressure, and the *acid* crystallises in colourless needles melting at $211\text{--}212^\circ$.

The sodium derivatives of the *o*- and *m*-hydroxy-esters were obtained by Freer's method (Abstr., 1893, i, 66), and that of the para-compound by the action of alcoholic sodium ethoxide on the ester and subsequent heating in a vacuum. J. J. S.

Isomeric Phenylparaconic Acids. By RUDOLPH FITTIG (*Ber.*, 1900, 33, 1294—1295. Compare Abstr., 1899, i, 437).—It has been shown that phenylitaconic acid is regenerated from phenylitaconic acid by the action of bromine in sunlight; in diffused light, however, a phenylbromoparaconic acid is formed, which, on reduction with sodium amalgam, yields an isomeride of phenylparaconic acid; this *isophenylparaconic acid* melts at 168° . Phenylparaconic acid is a racemic compound, and has been separated into its active components by means of the strychnine salts. R. H. P.

Acetylphenylacetylene and Benzoylphenylacetylene. By CHARLES MOUREU and RAYMOND DELANGE (*Compt. rend.*, 1900, 130, 1259—1261. Compare Nef, this vol., i, 20).—An aqueous solution of potassium hydroxide has no action on acetylphenylacetylene or benzoylphenylacetylene in the cold, but when boiling it hydrolyses the former into phenylacetylene and acetic acid, and the latter into benzoic acid

and acetophenone. Alcoholic potash yields the same compounds with benzoylphenylacetylene, whereas acetylphenylacetone is decomposed into tarry products. G. T. M

A Dihydrodisulphonic Acid derived from Carvone. By HENRI LABBÉ (*Bull. Soc. Chim.*, 1900, [iii], 23, 280—286).—Carvone does not yield a normal compound with sodium hydrogen sulphite, but when boiled for about an hour in a reflux apparatus with a solution of sodium hydrogen sulphite and sodium carbonate, it is completely dissolved with the formation of *sodium carvonedihydrodisulphonate*, $C_{10}H_{16}O_7S_2Na_2$. This compound, which was obtained as a deliquescent, white, or yellowish-white, powder, is not decomposed by alkalis and forms a *semicarbazone*, thus showing that the fixation of the sodium hydrogen sulphite is effected only by the ethylene linkings, the carbonyl group remaining unaltered.

The formation of this substance affords a means for the accurate estimation of carvone in essential oils, the oil unattacked by the sodium hydrogen sulphite solution being subsequently weighed and the carvone obtained by difference, or the sulphite utilised in the formation of the compound determined by titration with potassium iodide solution before and after the experiment. Limonene, which usually accompanies carvone in essential oils, also forms a dihydrodisulphonate derivative, an amorphous, white powder of the composition $C_{10}H_{16}(SO_3HNa)_2$; this is, however, formed with such difficulty, a yield of only 2 per cent. being obtained after 18 hours boiling with the sodium hydrogen sulphite solution, that the estimation of carvone by the process described is not appreciably affected thereby. N. L.

isoFenchyl Alcohol. By JULIUS BERTRAM and J. HELLE (*J. pr. Chem.*, 1900, [ii], 61, 293—306).—Fenchyl alcohol is best purified by conversion into, and subsequent hydrolysis of, *fenchyl hydrogen phthalate*, which crystallises from alcohol and melts at 145—145·5°. *Fenchyl formate* boils at 115° under 40 mm., and at 84—85° under 13 mm. pressure, has a sp. gr. 0·988 at 15°, and a rotation $\alpha_D - 73^\circ 14'$; *fenchyl acetate* boils at 87—88° under 10 mm. pressure, has a sp. gr. 0·9748 at 15°, and a specific rotation $[\alpha]_D - 58^\circ 08'$. *Fenchyl phenylurethane* forms broad needles or tablets melting at 82—82·5°.

The fenchene prepared by the authors according to Wallach's method (Abstr., 1891, 1088), using, however, quinoline instead of aniline, boiled at 154—156°, had a sp. gr. 0·8660—0·8665 at 15°, and a refractive index $[n]_D 1\cdot46733$ — $1\cdot46832$ at 17°.

isoFenchyl alcohol, prepared from fenchene in a similar manner to the preparation of *isoborneol* from camphene (Bertram and Walbaum, Abstr., 1894, i, 204), crystallises in colourless, flexible needles, melts at 61·5—62°, boils at 97—98° under 13 mm. pressure, has a sp. gr. 0·9613 at 15°, a refractive index $[n]_D 1\cdot48005$ at 15°, and a specific rotation in alcoholic solution $[\alpha]_D - 25^\circ 73'$. It is a saturated secondary alcohol and forms an *acetate*, which boils at 98—99° under 14 mm. pressure, and has a sp. gr. 0·974 at 15°. The acetate obtained from fenchene and glacial acetic acid boils at 89—90° under 8 mm. pressure, and has a sp. gr. 0·9724 at 15°. *isoFenchyl hydrogen phthalate*, prepared for the purification of the alcohol, is a colourless, crystalline powder,

melting at 149—150°. *isoFenchyl phenylurethane* crystallises from alcohol and melts at 106—107°. When treated with zinc chloride in benzene solution, *isofenchyl alcohol* yields a hydrocarbon, which is probably identical with fenchene. On oxidation with chromic acid, it yields a *ketone*, $C_{10}H_{16}O$, which boils at 193—194°, has a sp. gr. 0.950 at 15°, and a refractive index $[n]_D$ 1.46189, and forms an *oxime*, which crystallises in compact prisms melting at 82°; on reduction with sodium and alcohol, it yields an *alcohol*, which boils at 83—84° under 8 mm. pressure, and yields a *hydrogen phthalate*, which melts at 110—111°. R. H. P.

Camphane. By OSSIAN ASCHAN (*Ber.*, 1900, 33, 1006—1010).—In order to decide whether camphor yields an active or inactive camphane, $C_{10}H_{18}$, and thus to confirm one or other of the various formulæ which have been proposed for camphor, pinene hydriodide, which has been shown by Wagner and Brickner (this vol., i, 46) to be a true ether of borneol, was submitted to reduction. This is best carried out in acetic acid solution by means of zinc and hydriodic acid, when a perfectly inactive camphane is obtained, which crystallises in six-sided plates, and melts at 153—154°. The pinene hydriodide employed was only very faintly active, and it is possible that this was due to the presence of a small amount of an active impurity. A. H.

The Rendering Active of Oxygen. IV., V., and VI. By CARL ENGLER [and in part J. WEISSBERG] (*Ber.*, 1900, 33, 1090—1096, 1097—1109, 1109—1111. Compare *Abstr.*, 1897, ii, 402; 1899, i, 189, 221).—IV. *Autoxidation of oil of turpentine and of some other unsaturated compounds.*—When pure pinene is shaken with a measured quantity of $N/100$ sodium indigotindisulphonate in a flask containing air until decolorisation of the indigotin has been effected, it is found that the diminution in volume of the air corresponds approximately to twice the oxygen taken up by the indigotin; moreover, the diminution represents 4—5 atoms of oxygen for each molecule of pinene. This bears out the author's view that in such oxidations the oxygen gas is taken up by molecules at a time, peroxides being formed, which give up half their oxygen to substances capable of taking it—"acceptors," whilst the other half oxidises the substance that originally had absorbed the oxygen. Amylene, trimethylene-ethylene and hexylene absorb oxygen in a similar manner; when distilled, the products leave a residue which contains about two atoms of oxygen per mol. of the hydrocarbon.

V. *The phenomena of autoxidation* [with J. WEISSBERG].—Various cases of spontaneous oxidation in the presence of oxygen gas are considered from the authors' point of view (compare especially *Abstr.*, 1897, ii, 402, and above). They are regarded as conditioned by the unsaturated nature of the autoxidiser, or by the presence of labile hydrogen atoms in it, and the following categories are distinguished. (1) The oxygen adds itself on to unsaturated substances and forms peroxides (triethylphosphine, oil of turpentine, hexylene, &c.). (2) The oxygen unites with hydrogen, held in labile combination by the

autoxidiser, to form hydrogen peroxide; the remainder of the autoxidiser at once takes up another molecule of oxygen to form a peroxide (benzaldehyde, and probably palladium hydride). (3) The oxygen combines with labile hydrogen of the autoxidiser to form hydrogen peroxide; the remainder is not oxidisable, and either remains as it is, or suffers condensation; it may be a peroxide (hydroxides of alkalis and alkaline earths) or not (hydroxylamines, phenols, azo-compounds).

VI. *Demonstration of the formation of hydrogen peroxide and of other peroxides as products of direct oxidation.*—If a fine jet of burning hydrogen gas is directed against a small block of ice so as to bore a hole into the latter, hydrogen peroxide can be detected in the melted water by adding starch solution, potassium iodide, acid, and a trace of ferrous sulphate, or by shaking with ether and chromic acid; the hydrogen peroxide is cooled by the ice as soon as formed, and so protected from decomposition by the heat of the flame. To show that the peroxide does not result from decomposition of the water by the heat of the flame, a platinum wire rendered incandescent by an electric current is kept for several hours just at the surface of the water; no peroxide can then be detected in the latter. It can also be shown that hydrogen peroxide is formed when carbon monoxide, illuminating gas, alcohol, ether, carbon disulphide, &c., are burned in the same manner.

If sodium is burned on aluminium foil, and the product dissolved in water, hydrogen peroxide is found to be present. A peroxide is also formed when a very narrow, thin strip of magnesium ribbon is burned, or when a stouter piece is burned and held against ice or cold water.

C. F. B.

Parsley Oil. By CARLO BIGNAMI and GIUSEPPE TESTONI (*Gazzetta*, 1900, 30, i, 240—253).—The leaves and seeds of *Apium petroselinum* contain, besides apiol and the glucoside apiin, a dense, pale greenish-yellow oil, which boils at 277—285° under ordinary pressure, and has a sp. gr. 1.1206 at 17°. When fractionally distilled, the greater portion boils at 279—285°; it probably has the constitution

$\text{CH}_2 \begin{smallmatrix} \diagup \text{O} \\ \diagdown \text{O} \end{smallmatrix} \text{C}_6\text{H}_2(\text{C}_8\text{H}_5) \cdot \text{OMe}$. On further fractionating this portion

and determining the methoxy-groups in the different fractions, varying numbers were obtained. When oxidised with aqueous permanganate, the oil yields as principal product an acid identical with Roser's methylenemethylgallic acid (Abstr., 1890, 528) and with Semmler's myristicinic acid (Abstr., 1892, 311). Apiolic acid, trimethylgallic or methylsyringic acid, and a new *tetramethylapionol-carboxylic acid*, $\text{C}_{11}\text{H}_{14}\text{O}_6$, are also formed. The latter acid, which separates from light petroleum in stellate groups of large, white, acicular crystals melting at 87°, is readily soluble in benzene, acetone, ethyl acetate, methyl or ethyl alcohol, or boiling water. Its *silver* and *barium* (with $2\text{H}_2\text{O}$) salts are described. On heating with soda lime, the acid loses carbon dioxide, tetramethylapional being formed.

On brominating the original oil in acetic acid solution, an oily product and two isomeric *bromo*-derivatives of the composition

$C_{11}H_{10}O_3Br_4$, probably $CH_2\begin{smallmatrix} \diagup O \diagdown \\ \diagdown O \diagup \end{smallmatrix}C_6Br_2(OMe)\cdot CHBr\cdot CHMeBr$, are obtained. The first of these crystallises from alcohol in slender, silky needles melting at $131-134^\circ$, and is soluble in ethyl acetate; the *iso*-compound separates from alcohol in large, colourless crystals melting at 162° . T. H. P.

Constituents of West Indian Sandalwood Oil. By HUGO VON SODEN (*Chem. Centr.*, 1900, i, 858; from *Pharm. Zeit.*, 45, 229. Compare Abstr., 1899, i, 924).—By hydrolysing West Indian sandalwood oil from *Amyris balsamifera* with alcoholic potash, and fractionally distilling in a vacuum, a sesquiterpene alcohol, *amyrol*, $C_{15}H_{25}\cdot OH$, is obtained; it is an almost colourless liquid, of about the consistency of Venetian turpentine, has a faint aromatic odour and a bitter taste, boils at $299-301^\circ$ under 748 mm. and at $151-152^\circ$ under 11 mm. pressure, dissolves in $3-3\frac{1}{2}$ parts of 70 per cent. alcohol, and has a sp. gr. $0.980-0.982$ at 15° , and a rotatory power of about $+27^\circ$ (100 mm. tube). When heated with phthalic anhydride at 110° , it does not form an ester, but partially decomposes, losing water, and yielding a sesquiterpene. According to Dulière (*J. Pharm.*, 1898, [vi], 7, 553), West Indian sandalwood oil contains 42 per cent. of alcoholic constituents reckoned as santalol, but this result is low, for by the action of acetic anhydride only about 65 per cent. of the alcohol is converted into acetate, the rest forming a sesquiterpene. Amyrol, like santalol, may really consist of two similar alcohols of different rotatory power.

The oil also contains considerable quantities of sesquiterpenes, together with small quantities of substances which have strong odours. The former may be separated from the alcohols of higher boiling point by distilling the hydrolysed oil in a vacuum. E. W. W.

Santalenes and Santalols. By M. GUERBET (*Compt. rend.*, 1900, 130, 1324—1327. Compare this vol., i, 242).—When heated in sealed tubes with glacial acetic acid at $180-190^\circ$, α - and β -santalenes combine very slowly to form the *acetates* of santalene, $C_{15}H_{24}\cdot C_2H_4O_2$. The acetate of α -santalene boils at $164-165^\circ$, and the β -compound at $167-168^\circ$, the pressure in each case being 14 mm.

The *hydrochlorides*, $C_{15}H_{24}\cdot 2HCl$, are prepared by passing hydrogen chloride into a dry ethereal solution of the santalene; they are decomposed on distillation, even in a vacuum. The specific rotation of the α -compound is $+6^\circ$, whilst that of the β -compound is $+8^\circ$.

α -Santalene only yields one *nitrosochloride* when treated with nitrosyl chloride; this derivative crystallises from benzene in short prisms, and melts and decomposes at 122° . *α -Santalene nitrolepiperidine*, obtained by treating the nitrosochloride with a solution of piperidine in benzene, is readily soluble in alcohol, and crystallises in needles melting at $108-109^\circ$.

Two *nitrosochlorides* are produced from β -santalene; these are separated from each other by fractional crystallisation from alcohol; the less soluble melts at 152° , and the other, which forms the main product of the reaction, melts at 106° ; the corresponding *nitroleamines* melt at 101° and $104-105^\circ$ respectively.

The yield of nitrosochloride is greatly increased by operating in solutions of light petroleum cooled with ice and salt, the amount obtained being about 50 per cent. of the theoretical. Wallach's method of preparation gives very poor results in the case of the santalenes.

α -Santalol, $C_{15}H_{26}O$, is a colourless, oily liquid with a faint odour, boiling at $162-163^\circ$ under 13 mm. and at $300-301^\circ$ under normal pressure; it has a sp. gr. 0.9854 at 0° and $[\alpha]_D - 1.2^\circ$.

β -Santalol resembles its isomeride, and boils at $170-171^\circ$ under 14 mm. and at $309-310^\circ$ under normal pressure; it has a sp. gr. 0.9868 at 0° and $[\alpha]_D - 56^\circ$.

The acetates, $C_{15}H_{25} \cdot OAc$, are colourless, oily liquids; the α -compound boils at $308-310^\circ$, and the β -compound at $316-317^\circ$.

Determinations of the velocities and limits of esterification indicate that the santalols are primary alcohols, these constants being respectively 41.7 and 68.5 for the α -compound and 43.6 and 69 for the β -isomeride. It follows that the hydroxyl group of these alcohols is not attached to a carbon atom of the ring.

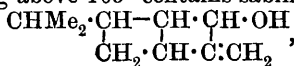
The santalols, when treated with dehydrating agents, such as potassium hydrogen sulphate or phosphoric oxide, are converted into two isomeric hydrocarbons, for which the name *isosantalene* is proposed. These substances are colourless liquids, having an odour of turpentine; the α -derivative boils at $255-256^\circ$, and has $[\alpha]_D + 0.2^\circ$; the β -isomeride boils at $259-260^\circ$, and has $[\alpha]_D + 6.1^\circ$.

G. T. M.

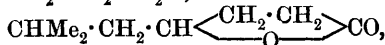
Oil of Savin (*Oleum Sabinae*). II. By EMIL FROMM [in part with W. LISCHKE] (*Ber*, 1900, 33, 1191-1211; *Abstr.*, 1898, i, 674).—A large quantity of the oil was hydrolysed by boiling it with just the necessary quantity of potassium hydroxide and enough alcohol to bring everything into solution; the product was steam distilled. The residual liquid contained chiefly a little acetic acid, but also small quantities of an acid, $?C_{18}H_{34}O(CO_2H)_2$, boiling at 255° , of which the *magnesium* salt was analysed, and of another acid, $?C_{11}H_{13}O_2(CO_2H)_3$, which boils at about 260° and melts at 181° .

The oil which distilled over with the steam was fractionated; the portion boiling below 165° , equal to about 25 per cent. of the oil, consisted mainly of a terpene, $C_{10}H_{16}$, boiling at 158° ; this has not yet been identified.

The portion boiling above 165° contains sabinol,



which yields α -tanacetogendicarboxylic acid, $CHMe_2 \cdot \underset{\text{CH}_2}{\underset{|}{CH}} - \underset{\text{CH}_2}{\underset{|}{CH}} \cdot CO_2H$
 $\underset{\text{CH}_2}{\underset{|}{CH}} \cdot \underset{\text{CH}_2}{\underset{|}{CH}} \cdot CO_2H$,
 on oxidation. When this acid is heated, it loses carbon dioxide and forms an acid and a lactone, recognised as $\gamma\delta$ -isooctenic acid, $CHMe_2 \cdot \underset{\text{CH}_2}{\underset{|}{CH}} : \underset{\text{CH}_2}{\underset{|}{CH}} \cdot CH_2 \cdot CH_2 \cdot CO_2H$, and isooctolactone,



respectively, because the lactone yields a β -hydroxyisovalerate when it is oxidised with permanganate in cold alkaline solution; the acid

yields succinic acid, in addition to volatile acids and a little oxalic acid, when it is oxidised with permanganate in the cold. When sabinol is heated with 10 per cent. alcoholic hydrochloric acid for a little while, *p*-cymene is formed as the chief product. These reactions lead to the adoption of the formulæ given above. C. F. B.

Indigo Fermentation. By MARTINUS BEIJERINCK (*Proc. K. Akad. Wetensch. Amsterdam*, 1900, 2, 495—512. Compare this vol., i, 230).—The expression “indigo fermentation” includes two distinct processes, one a katabolic change brought about by the direct action of living protoplasm, the other a decomposition induced by enzymes; in either case, this action can only take place in indigo plants; there can be no fermentation in woad (*Isatis tinctoria*), a plant which contains free indoxyl, but no indigo yielding glucoside.

The preparation of indican and indigo enzyme from *Polygonum tinctorium* and *Indigofera leptostachya* is described in detail. These substances accumulate more particularly in the leaves, and to a less extent in the flowers; they are, however, absent from the roots, stems, and reproductive cells. Microchemical examination of the leaves of *Phajus grandiflorus* showed that the indican is present in the protoplasm, but not in the sap nuclei and cell-walls; the chlorophyll granules contain indigo enzyme, but no glucoside. Indigo enzymes are very seldom found elsewhere than in the indigo plants, but indican is decomposed by emulsin from almonds; glucase from maize, although resembling this enzyme in its action on amygdalin, does not hydrolyse indican. It is found that the indigo enzymes from *Indigofera*, emulsin, *Phajus*, *Saccharomyces sphæricus*, and *Polygonum* are specifically different, having respectively the following temperature optima, 61°, 55°, 53°, 44°, and 42°.

In *Indigofera*, the fermentation is entirely due to enzymes; in *Polygonum* and *Phajus* the action is partly katabolic.

When indican is hydrolysed by bacteria, the action is katabolic, hence the dead organisms have no action on the glucoside.

G. T. M.

Indican and its Enzyme. By J. J. HAZEWINKEL (*Proc. K. Akad. Wetensch. Amsterdam*, 1900, 2, 512—520. Compare preceding abstract).—When the leaves of *Indigofera leptostachya* are extracted with boiling water or dilute solutions of calcium hydroxide or mercuric chloride, a solution is obtained which contains an indigo yielding glucoside. The production of indigotin may be brought about by the action of (1) oxidising agents in acid solutions, (2) enzymes derived from the indigo plant or other sources, (3) bacteria. The enzyme from *Indigofera* was obtained by extracting the leaves with concentrated alcohol, drying the residue at the ordinary temperature, and employing it in the form of powder; the active principle contained in the preparation is somewhat soluble in water, but more so in 10 per cent. brine solution.

The glucoside contained in the aqueous extract was not isolated, but it appears to have some properties in common with indican. Indoxyl is formed as an intermediate product in the formation of indigo, confirmatory proof of its presence being obtained by the production of

the indogenides of isatin, benzaldehyde, and pyruvic acid. The presence of indoxyl in the products of hydrolysis accounts for the large amount of indigo-red which is formed in some processes of indigo manufacture.

G. T. M.

Indican. By SEBASTIAAN HOOGEWERFF and H. TER MEULEN (*Proc. K. Akad. Wetensch. Amsterdam*, 1900, 2, 520—525. Compare preceding abstracts).—Indican may be obtained from indigo leaves in colourless, spear-shaped crystals by treating an aqueous decoction with barium hydroxide, filtering off impurities, removing excess of the base with carbon dioxide, evaporating the filtrate to dryness, extracting the crude residue with methyl alcohol, adding ether to the extract to precipitate the last traces of foreign substances, distilling off these solvents, dissolving the final residue in water, and allowing the solution to deposit the glucoside. It crystallises with $3\text{H}_2\text{O}$, melts at 51° , and passes into a gummy mass at 100° . When dried in a vacuum over sulphuric acid, indican loses its water of crystallisation, and then melts at 100 — 102° . Ultimate analysis and cryoscopic molecular weight determinations point to the formula $\text{C}_{14}\text{H}_{17}\text{NO}_6$, thus confirming Marchlewski and Radcliffe's hypothesis (*Abstr.*, 1899, i, 387). The glucoside is moderately soluble in water, acetone, or the alcohols, and has a bitter taste; a 2 per cent. solution in a 20 cm. tube at 15° gives a rotation of -2° ; after hydrolysis and the formation of indigotin, the liquid becomes dextrorotatory. When air is passed through a solution of indican in dilute hydrochloric acid containing a little ferric chloride, 91 per cent. of the glucoside is converted into indigotin, according to the following equation, $2\text{C}_{14}\text{H}_{17}\text{NO}_6 + \text{O}_2 = \text{C}_{16}\text{H}_{10}\text{N}_2\text{O}_2 + 2\text{C}_6\text{H}_{12}\text{O}_6$, a certain amount of indigo-red being simultaneously produced.

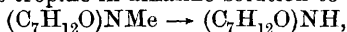
The indican from *Indigofera leptostachya* appeared to be identical with that from *Polygonum tinctorium*.

G. T. M.

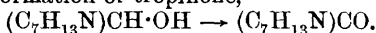
Chemistry of Chlorophyll: Phyllorubin. By LEO MARCHLEWSKI (*J. pr. Chem.*, 1900, [ii], 61, 289—292).—When phyllocyanin (*Abstr.*, 1894, i, 341) is heated with alcoholic potash until the alcohol is nearly all evaporated, a viscous, green mass is obtained; this is dissolved in water, acidified and extracted with ether, when the ethereal solution yields an amorphous substance, *phyllorubin*, which shows a spectrum different from that given by phylloporphyrin (*Abstr.*, 1895, i, 297) or phyllotaonin (*Abstr.*, 1896, i, 181).

R. H. P.

Action of Potassium Permanganate on Bases. By RICHARD WILLSTÄTTER (*Ber.*, 1900, 33, 1167—1170).—Whilst potassium permanganate oxidises tropine in alkaline solution to tropigenin,



in acid solution, the basic group is protected and the $\cdot\text{CH}(\text{OH})\cdot$ group is attacked with formation of tropinone,



Lead dioxide in sulphuric acid behaves similarly.

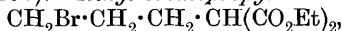
T. M. L.

Reduction of Tropinone to Tropine and Tropane. By RICHARD WILLSTÄTTER and FRITZ IGLAUER (*Ber.*, 1900, 33, 1170—1176).—Tropine and ψ -tropine can be readily separated by means of their

picrates. Tropine picrate crystallises in long trapezoid forms or striated, six-sided tablets, darkens at 270° , and decomposes at 275° without melting; 0.462 part dissolves in 100 parts of water at 16° ; ψ tropine picrate crystallises in long, pointed needles, begins to decompose at 245° , and melts at $258-259^{\circ}$; 1.484 parts dissolve in 100 parts of water at 14° .

By reducing tropinone with zinc dust and hydriodic acid at 0° , it is converted into a mixture of tropine and ψ -tropine, together with a smaller amount of tropane; the conversion of the ψ -tropine, stable towards alkali, into the labile tropine can thus be readily effected by oxidising to tropinone and then reducing. If the reduction is carried out at 50° , the yield of tropane is doubled. T. M. L.

Synthesis of Hygic Acid. By RICHARD WILLSTÄTTER (*Ber.*, 1900, 33, 1160—1166).—*Ethyl bromopropylmalonate*,



prepared by the action of trimethylene bromide on ethyl sodiomalonate, boils at $158-160^{\circ}$ under 14 mm. pressure.

By the action of bromine, it is converted into *ethyl α -dibromopropylmalonate*, $\text{CH}_2\text{Br}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{CBr}(\text{CO}_2\text{Et})_2$; this boils at 177° under 11 mm. pressure, and, when treated with ammonia, gives an *amide*,

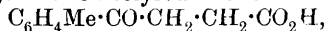
$\text{CH}_2\begin{matrix} \text{CH}_2\cdot\text{NH} \\ \diagup \\ \text{CH}_2\cdot\text{C}(\text{CO}\cdot\text{NH}_2)_2 \end{matrix}$, which crystallises in rhombic tablets, melts at 163° , and is hydrolysed by hydrochloric acid or baryta to 2-pyrrolidinecarboxylic acid which melts at 198° , gives an *ethyl* ester which boils at $75-76^{\circ}$ under 11 mm. pressure, and closely resembles hygic acid. The chief product of the action of methylamine is a *methylamide*, probably $\text{CH}_2\begin{matrix} \text{CH}_2\cdot\text{CH}_2 \\ \diagup \\ \text{NMe}\cdot\text{CO} \end{matrix}\text{C}\begin{matrix} \diagdown \\ \text{CO}\cdot\text{NHMe} \\ \diagup \\ \text{NHMe} \end{matrix}$, which crystallises in monoclinic prisms, melts at 124° , and when hydrolysed with baryta loses only 1 mol. of methylamine, giving rise to a substance which is regarded as the lactam of α -dimethyldiaminovaleric acid, a methylaminomethyl-2-piperidone, $\text{CH}_2\begin{matrix} \text{CH}_2\cdot\text{CH}_2 \\ \diagup \\ \text{NMe}\cdot\text{CO} \end{matrix}\text{CH}\cdot\text{NHMe}$. The pyrrolidine compound is only produced in small quantities by the action of methylamine, but was isolated in the form of *ethyl 1-methylpyrrolidine-2:2-dicarboxylate*,

$\begin{matrix} \text{CH}_2\cdot\text{NMe} \\ \diagup \\ \text{CH}_2\cdot\text{CH}_2 \end{matrix}\text{C}(\text{CO}_2\text{Et})_2$, which boils at $133-135^{\circ}$ under 16 mm. pressure; from the product of hydrolysis, there was also

isolated *1-methylpyrrolidine-2-carboxylic acid*, $\begin{matrix} \text{CH}_2\cdot\text{NMe} \\ \diagup \\ \text{CH}_2\cdot\text{CH}_2 \end{matrix}\text{CH}\cdot\text{CO}_2\text{H}$, which was found to be identical with Liebermann and Cybulski's hygic acid (*Abstr.*, 1895, i, 310), the constitution of which is thus finally established. T. M. L.

Action of Phenylcarbimide and Aniline on γ -Ketonic Acids.

—By TIMOTHÉE KLOBB (*Compt. rend.*, 1900, 130, 1254—1256. Compare *Abstr.*, 1899, i, 510).—When tolylbutanonic acid,



is heated at 200° with phenylcarbimide, the compound $\text{C}_{34}\text{H}_{30}\text{N}_2\text{O}_2$, a

polymeride of the pyrrolone $C_7H_{15}NO$, is produced, together with a small amount of the *anilide* of the acid. The former substance crystallises in golden-yellow needles melting at 204° , and the latter in nacreous leaflets melting at 147° .

Triphenylbutenolide (triphenylcrotonolactone), $CH \begin{smallmatrix} \swarrow CPh-O \\ \searrow CPh_2 \cdot CO \end{smallmatrix}$, obtained by heating triphenylbutanonoic acid, $COPh \cdot CH_2 \cdot CPh_2 \cdot CO_2H$, with the same reagent at 100° , is identical with the substance obtained by Japp and Klingemann (Trans., 1890, 57, 678).

Tetraphenylpyrrolone, $CH \begin{smallmatrix} \swarrow CPh-NPh \\ \searrow CPh_2 \cdot CO \end{smallmatrix}$, prepared by heating triphenylbutanonoic acid with aniline in sealed tubes at $180-200^\circ$, crystallises from benzene in monoclinic prisms containing 1 mol. of the solvent, and melting at 115° . The compound is dimorphous, for it crystallises from alcohol both in hexagonal and monoclinic prisms, the former melting at $123-124^\circ$, the latter at $133-134^\circ$ (compare Tutton, Trans., 1890, 57, 714).

The γ -lactone, $COPh \cdot CH_2 \cdot CH \begin{smallmatrix} \swarrow CO-O \\ \searrow CH : CPh \end{smallmatrix}$, of diphenacylacetic acid, $CH(CH_2 \cdot COPh)_2 \cdot CO_2H$, produced from this substance with phenylcarbimide, melts at 162° ; when heated with carbanilide, it is decomposed without yielding either an anilide or a pyrrolone. The latter, 1:2-diphenyl-4-phenacylpyrrolone, $COPh \cdot CH_2 \cdot CH \begin{smallmatrix} \swarrow CO \cdot NPh \\ \searrow CH : CPh \end{smallmatrix}$, is obtained by the direct action of aniline on the acid; it melts at 140° . A polymeride, $C_{48}H_{38}O_4N_2$, of this pyrrolone is sometimes obtained in this condensation; it is a well-defined, red substance, which, when crystallised from alcohol, undergoes a partial transformation into a colourless derivative melting at 280° and having an acid reaction.

G. T. M.

Addition of Formaldehyde to 2:4-Lutidine. Decomposition of 2:4-Lupetidine into its Optical Isomerides. By OTTO ENGELS (Ber., 1900, 33, 1087—1090).—When 2:4-lutidine is heated with 40 per cent. formaldehyde solution at $135-140^\circ$, 2:4-lutidylalkine [2-hydroxyethyl-4-methylpyridine], $CH \begin{smallmatrix} \swarrow CMe \cdot CH \\ \searrow CH = N \end{smallmatrix} C \cdot CH_2 \cdot CH_2 \cdot OH$, is formed. This boils at $130-132^\circ$ under 16 mm. pressure; its *platini-chloride* and *aurichloride* were analysed.

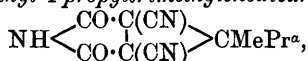
Inactive 2:4-lupetidine, obtained by reducing 2:4-lutidine with sodium and absolute alcohol, was mixed with the equivalent amount of *a*-tartaric acid in aqueous solution, and the solution concentrated; crystals melting at $49-50^\circ$ separated, and from these the *d*-lupetidine was obtained, with a specific rotation $[\alpha]_D + 23.17^\circ$. By regenerating the base from the mother liquor and treating it with *l*-tartaric acid, a salt was obtained which melted at $49-50^\circ$; from this, the *l*-lupetidine was isolated with a specific rotation $[\alpha]_D - 21.0^\circ$.

C. F. B.

Synthesis of Glutaric and Trimethylene Derivatives. By A. MINOZZI (Gazzetta, 1900, 30, i, 265—278. Compare Guareschi and Grande, this vol., i, 111; and Pasquali, Abstr., 1898, i, 272).—

3 : 5-Dicyano-2 : 6-dioxy-4-methyl-4-propylpiperidine (αα-dicyano-ββ-methylpropylglutarimide), $\text{NH} \begin{smallmatrix} \text{CO} \cdot \text{CH}(\text{CN}) \\ \text{CO} \cdot \text{CH}(\text{CN}) \end{smallmatrix} \text{CMePr}^\alpha$, obtained as its ammonium derivative by the action of methyl propyl ketone on ethyl cyanoacetate in presence of alcoholic ammonia, separates from acetic acid in fine, large, transparent laminae melting at 201—202°; it gives a yellow coloration with potassium nitrite and sulphuric acid, and is soluble in alcohol or ether, or in boiling water, to which it gives an acid reaction. Its ammonium salt, $\text{C}_{11}\text{H}_{16}\text{O}_2\text{N}_4$, is a white, crystalline compound soluble in water; it loses ammonia even at the ordinary temperature, and melts and decomposes at 192—193°; the aqueous solution loses hydrogen cyanide and propane slowly on standing, more quickly on heating, with the formation of the ammonium derivative of methyl dicyanoglutarimide, crystallising in beautiful needles, which on heating lose ammonia, and do not melt at 310°. The silver salt, $\text{C}_{11}\text{H}_{12}\text{O}_2\text{N}_3\text{Ag}$, is a white, flocculent precipitate. The dibromo-derivative, $\text{C}_{11}\text{H}_{11}\text{O}_2\text{N}_3\text{Br}_2$, is a white compound soluble in boiling water, alcohol, or 50 per cent. acetic acid; on heating, it loses bromine and melts and decomposes at 170—173°.

3 : 5-Dicyano-4-methyl-4-propyltrimethylenedicarbonimide,



obtained on heating the dibromo-derivative with 50 per cent. acetic acid, crystallises from acetic acid in thin, white plates, or from water in hard, colourless needles, begins to decompose at 175°, melts at 183°, gives an acid aqueous solution, yields no coloration with potassium nitrite and sulphuric acid, but forms soluble salts with the alkali and alkaline earth metals, and with mercuric chloride and lead acetate gives white, flocculent precipitates insoluble in boiling water. Its silver salt, $\text{C}_{11}\text{H}_{10}\text{O}_2\text{N}_3\text{Ag}$, is a white, flocculent precipitate which is turned brown by light, and decomposes in boiling water. On hydrolysing the imide with aqueous sodium hydroxide, ammonia is evolved, and the sodium salt of 1-methyl-1-propyltrimethylene-2 : 3-dicyanodicarboxylic acid, $\text{CMePr}^\alpha \begin{smallmatrix} \text{C}(\text{CN}) \cdot \text{CO}_2\text{H} \\ \text{C}(\text{CN}) \cdot \text{CO}_2\text{H} \end{smallmatrix}$, formed; the acid separates from alcohol in a crystalline mass melting at 116—119°; its silver salt, $\text{C}_{11}\text{H}_{10}\text{O}_4\text{N}_2\text{Ag}_2$, forms a white, gelatinous mass readily decomposable by the action of light or heat.

The action in the cold of methyl isopropyl ketone (1 mol.) on ethyl cyanoacetate (2 mols.) in presence of alcoholic ammonia (3 mols.) gives rise to cyanoacetamide, but if aqueous ammonia is employed, or if the above mixture is heated at 85—90° in a reflux apparatus, 3 : 5-dicyano-2 : 6-dioxy-4-methyl-4-isopropylpiperidine (αα-dicyano-ββ-methylisopropylglutarimide), $\text{NH} \begin{smallmatrix} \text{CO} \cdot \text{CH}(\text{CN}) \\ \text{CO} \cdot \text{CH}(\text{CN}) \end{smallmatrix} \text{CMePr}^\beta$, is obtained; it separates from dilute hydrochloric acid in flocculent aggregates of minute, white needles, or from alcohol in large, colourless, transparent plates melting at 232—234°, and is soluble in glacial acetic acid, and to a slight extent in water, forming an acid solution. Its ammonium salt is unstable, the aqueous solution decomposing with the formation of

the ammonium salt of methylidyne-glutarimide and evolution of propane. The *silver* salt, $C_{11}H_{12}O_2N_3Ag$, forms a white, flocculent precipitate. The *dibromo-derivative*, $C_{11}H_{11}O_2N_3Br_2$, separates from water in flocculent masses of small, white needles melting and decomposing at $163-165^\circ$; it dissolves in alcohol, ether, or acetic acid. 3:5-Dicyano-4-methyl 4-isopropyltrimethylenedicarbonimide, $C_{11}H_{11}O_2N_3$, which is obtained on heating the bromo-derivative with dilute acetic acid, separates in brilliant, colourless prisms melting and decomposing at about 240° ; it dissolves slightly in water, giving an acid solution which gives no coloration with potassium nitrite and sulphuric acid, and does not yield any gas when neutralised with ammonia. Its *silver* salt, $C_{11}H_{10}O_2N_3Ag$, is a white, flocculent precipitate which is moderately soluble in water and is decomposed by the action of light or heat.

T. H. P.

2-Methylketole. By R. VON WALTHER and J. CLEMEN (*J. pr. Chem.*, 1900, [ii], 61, 249—289).—2-Methylketole condenses with aldehydes to

form well-characterised compounds of the type $CHR\left(C\begin{smallmatrix} \text{CMe} \\ \text{C}_6\text{H}_4 \end{smallmatrix} > NH\right)_2$.

Methylene-bis-2-methylketole is a white, microcrystalline powder which melts at $230-231^\circ$; *p-methoxybenzylidene-bis-2-methylketole* is a faint reddish, microcrystalline powder which melts at 206° ; *o-hydroxybenzylidene-bis-2-methylketole* is a white, crystalline powder which melts at 224° ; *isopropylbenzylidene-bis-2-methylketole* is a white, microcrystalline powder which melts at 220° and turns red on exposure to light; *p-nitrobenzylidene-bis-2-methylketole* is a yellowish-red, microcrystalline powder which melts at 236° ; and *o-nitrobenzylidene-bis-2-methylketole* is a yellowish, microcrystalline powder which melts at 229° .

Ethyl acetoacetate condenses with 2-methylketole to form the *compound*, $CO_2Et \cdot CH_2 \cdot CMe\left(C\begin{smallmatrix} \text{CMe} \\ \text{C}_6\text{H}_4 \end{smallmatrix} > NH\right)_2$, which is a pale yellow, amorphous powder melting at 158° . Phenylcarbimide and 2-methylketole condense to form the *compound*, $CH\begin{smallmatrix} \text{CMe} \\ \text{C}_6\text{H}_4 \end{smallmatrix} > N \cdot CO \cdot NHPh$, which forms silvery leaflets melting at 170° . *Mononitro-2-methylketole*, best prepared by the action of a mixture of 100 per cent. nitric acid and concentrated sulphuric acid on 2-methylketole, forms compact, yellow prisms which melt at 170° ; it condenses with formaldehyde to *methylene-bis-nitro-2-methylketole*, which is a yellow, microcrystalline powder melting at 131° , and with benzaldehyde to *benzylidene-bis-nitro-2-methylketole*, which is a yellow, microcrystalline powder melting at 291° .

When heated with nitric acid of sp. gr. 1.38, 2-methylketole yields *dinitro-2-methylketole*, which forms brownish-yellow, lustrous, microcrystalline powder melting at 268° , and a brown, amorphous substance melting at $277-278^\circ$. Nitro-2-methylketole is only attacked with great difficulty by reducing agents; treatment with tin and hydrochloric acid for 3 hours gives a small yield of *amino-2-methylketole*; this is precipitated from benzene by light petroleum in the form of a colourless, light, voluminous substance, which melts at 137° and yields an amorphous *acetyl* derivative melting at 188° . 2-Methylketolephenylcarbamide and

2-methylketolephenylthiocarbamide are white, amorphous powders which melt respectively at 194° and 162°.

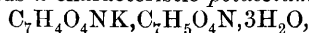
R. H. P.

2-Methylpyridine-6-carboxylic Acid. By ALBERT LADENBURG and K. SCHOLTZE (*Ber.*, 1900, 33, 1081).—2-Methylpyridine-6 carboxylic acid, $C_7H_7O_2N$, is prepared by oxidising 2:6-lutidine with three times its weight of potassium permanganate in 3 per cent. solution at 50–60°, and is isolated by means of its copper salt. It crystallises in colourless, lustrous needles, and is readily soluble even in cold water. The air-dried substance contains $1H_2O$ and melts at 95°. The copper salt, $(C_7H_6NO_2)_2Cu \cdot H_2O$, forms bright blue, well-formed crystals, is sparingly soluble in hot water, and decomposes at 252–253°.

A. L.

Pyridinecarboxylic Acids. By ADOLF PINNER (*Ber.*, 1900, 33, 1225–1230).—The author has examined fractions of pyridine bases of different boiling points obtained from coal tar, by oxidising them with aqueous potassium permanganate and separating the mixed carboxylic acids by means of their copper salts, according to Weidel's method. The fraction boiling at 128–134° consists almost entirely of α -picoline, and can be used as a source of α -picolinic acid; that boiling at 137–142° contains only a small quantity of α -picoline, with larger, almost equal, quantities of β - and γ -picoline, along with much 2:6-dimethylpyridine; this fraction can be used as a source of nicotinic and isonicotinic acids.

The hitherto undescribed 2-methylpyridine-6-carboxylic acid, obtained in the oxidation of the fraction boiling at 135–142°, is characterised by its great solubility in water and alcohol, and can be purified by crystallisation from benzene (see following abstract). Pyridine-2:6-dicarboxylic acid yields a characteristic potassium salt,



which forms beautiful, long, slender needles.

The esters of pyridinecarboxylic acids combine readily with ethyl acetate in presence of sodium ethoxide to form crystalline sodium derivatives of the type $C_5NH_4 \cdot C(ONa) : CH \cdot CO_2Et$; ethyl α - and β -pyridoylacetates, obtained from the corresponding sodium derivatives, are oils which decompose on distillation under reduced pressure; ethyl γ -pyridoylacetate, on the other hand, is a solid which can readily be purified. These compounds will be dealt with in a subsequent communication.

W. A. D.

2-Methylpyridine-6 carboxylic Acid By ADOLF PINNER and J. LEWIN (*Ber.*, 1900, 33, 1230–1231).—This acid (preceding abstract) forms long, white, lustrous needles, and melts at 84–85°; the hydrochloride forms leaflets melting at 138°, and the acid sulphate, $C_7H_7O_2N, H_2SO_4$, highly lustrous, hexagonal prisms, sparingly soluble in cold alcohol. The barium salt forms shining leaflets; the copper salt, with $2H_2O$, forms beautiful, bluish-green, pointed prisms, whilst with $1H_2O$ it crystallises in blue plates. The acid on oxidation yields pyridine-2:6-dicarboxylic acid.

W. A. D.

Conversion of Diethyl Lutidinedicarboxylate into Diaminolutidine. By ERNST MOHR (*Ber.*, 1900, 33, 1114–1120).—The

dihydrazide, $C_5NHMe_2(CO \cdot NH \cdot NH_2)_2$, obtained by warming ethyl lutidinedicarboxylate [$Me_2 : (CO_2Et)_2 = 2 : 6 : 3 : 5$] (Knoevenagel and Klages, *Annalen*, 1894, 281, 94) with hydrazine hydrate, crystallises from alcohol in thin, colourless prisms, and melts with slight decomposition at 228° ; from water, needles with $1H_2O$ are obtained; the *hydrochloride*, $C_9H_{13}O_2N_5 \cdot 3HCl \cdot H_2O$, melts and decomposes at 251° . The β -*propylidene* (acetone) derivative, $C_5NHMe_2(CO \cdot NH \cdot N : CMe_2)_2$, is a white powder which melts and decomposes at 298° ; the analogous *dibenzylidene* derivative, $C_{23}H_{21}O_2N_5$, crystallises from glacial acetic acid, and does not melt at 300° . *Lutidinedicarboxylodiazouimide*, $C_5NHMe_2(CO \cdot N < \begin{smallmatrix} N \\ | \\ N \end{smallmatrix})_2$, obtained by the action of nitrous acid at 0°

on the foregoing hydrazide, is a white powder which explodes at $79-80^\circ$, and, when heated with absolute alcohol, yields **diurethyl-lutidine*, $C_5NHMe_2(NH \cdot CO_2Et)_2$; this forms stout, transparent prisms, melts at 157° , and on being heated with hydrochloric acid for 5 hours at $100-120^\circ$, yields *diaminolutidine dihydrochloride*, $C_5NHMe_2(NH_2)_2 \cdot 2HCl \cdot H_2O$ [$Me_2 : (NH_2)_2 = 2 : 6 : 3 : 5$]. This, salt when heated at 110° , gives rise to the *hydrochloride*, $C_7H_{11}N_3 \cdot HCl$, which darkens at 265° , and melts and decomposes at $275-280^\circ$; on crystallising the dihydrochloride from boiling water, long, slender, felted needles of the *salt*, $C_7H_{11}N_3 \cdot HCl \cdot H_2O$, are obtained, which blacken at 280° and melt and decompose at 290° . The *base*, $C_5NHMe_2(NH_2)_2$, crystallises from benzene in feebly yellow prisms, and melts at $169-170^\circ$.
W. A. D.

Solubilities of Osazones. By CARL NEUBERG (*Zeit. Physiol. Chem.*, 1900, 29, 274-280).—It is a well-known fact that it is impossible to isolate from diabetic urine an amount of phenyl-glucosazone corresponding with the amount of sugar determined by polarimetric or titrimetric methods. The author concludes that this is due to the fact that the osazones are more soluble in liquids rich in nitrogen compounds than they are in water. This has been proved in the case of the amount of osazone from dextrose and from lævulose. According to Maquenne (*Abstr.*, 1891, 1142), in one hour at 100° under fixed conditions 1 gram of dextrose yields 0.32, and the same amount of lævulose 0.72, gram of osazone; the author finds that, when the same conditions are employed, with the exception that urine is used instead of water for washing, 1 gram of dextrose yields 0.186 gram of osazone and 1 gram of lævulose 0.432 gram of osazone.

Further experiments have shown that ammonia, amines, ammonium compounds, and most nitrogen derivatives increase the solubility of osazones in water or in alcohol.

In the estimation of sugars in urine, etc., it is therefore advisable to remove as far as possible the nitrogen compounds before precipitating with phenylhydrazine. Amino-acids, &c., can usually be removed in the form of silver, lead, or copper salts, and carbamide by the careful addition of alkali nitrate and acetic acid. J. J. S.

* The author suggests the name *urethyl* for the radicle $\cdot NH \cdot CO_2Et$.

Hydrazones of Dithiocarbonates. By MAX BUSCH and EDMUND LINGENBRINK [and in part H. HOLZMANN] (*J. pr. Chem.*, 1900, [ii], 61, 336—344. Compare this vol., i, 66). The *phenylhydrazone* of *methyl o-nitrobenzyl dithiocarbonate* forms large, lustrous, orange-coloured needles, which melt at 60—61°. The *diphenylhydrazone* of *dimethyl methylene dithiodicarbonate*, obtained by the action of ethylene dibromide on methyl phenyldithiocarbazine, forms lustrous, brittle needles which melt at 113—114°. The corresponding *p*-tolylhydrazones are oils.

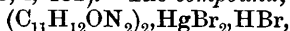
Potassium *p*-bromophenyldithiocarbazine reacts with methyl iodide, forming *methyl p-bromophenyldithiocarbazine*, which crystallises in small needles melting at 158—159°, and on treatment with methyl iodide yields the *p-bromophenylhydrazone* of *dimethyl dithiocarbonate*, which forms compact, brownish crystals melting at 48—49°. The *p-bromophenylhydrazone* of *ethylene dithiocarbonate* forms small, colourless needles melting at 141°. *Methyl hydrogen benzoylphenyldithiocarbazine* forms lustrous, small needles, which turn brown at 200°, melt and froth at 202°; on treatment with methyl iodide, it yields the *benzoylphenylhydrazone* of *dimethyl dithiocarbonate*, which crystallises in four-sided columns melting at 110—111°. *Benzyl acetylphenyldithiocarbazine* crystallises in small, yellow needles melting at 154°, and yields an oil on treatment with methyl iodide.

The phenylhydrazone of ethylene dithiocarbonate, on hydrolysis with dilute sulphuric acid, yields ketomethylene ethylene disulphide (Husemann, *Annalen*, 1863, 126, 269), which softens at 35° and melts at 39° (not 31°).
R. H. P.

Action of α -Acylated Phenylhydrazines on the Chlorine Derivatives of Quinones. By WILLIAM MCPHERSON and ROBERT FISCHER (*J. Amer. Chem. Soc.*, 1900, 22, 141—144).— *α -Benzoylphenylhydrazinotrichloroquinone*, $C_6Cl_3O_2 \cdot NH \cdot NBzPh$, obtained by the action of α -benzoylphenylhydrazine on trichloroquinone, crystallises in bright red, rectangular prisms, is readily soluble in hot benzene or alcohol, sparingly so in light petroleum, and melts at 158·5°. It reacts with phenylhydrazine, but decomposition occurs with evolution of gas. By the action of concentrated sulphuric acid or alcoholic potassium hydroxide, the benzoyl group is eliminated, and a crystalline product obtained which is soluble in sodium hydroxide and melts and decomposes at 198°.

α -Benzoylphenylhydrazinotrichloroquinone is also produced when α -benzoylphenylhydrazine is heated with tetrachloroquinone, hydrogen chloride being evolved.
E. G.

New Mercuric Haloid Derivatives of Antipyrine. By JULES VILLE and CHARLES ASTRE (*Compt. rend.*, 1900, 130, 1256—1258. Compare Abstr., 1898, i, 482).—The compound,



produced by adding dilute acetic acid to an aqueous solution of mercuric and potassium bromides and antipyrine, crystallises in lamellæ and rhombohedral plates, melts at 115—116°, and is slightly soluble in water, alcohol, or chloroform. Concentrated sulphuric

acid, alone or mixed with manganese dioxide, causes an evolution of hydrogen bromide, but bromine is not liberated. The compound ($C_{11}H_{12}ON_{2/2}, HgI_2, HI$), obtained in a precisely similar manner, melts at $119-120^\circ$, and is very slightly soluble in water, dissolving somewhat more readily in alcohol and chloroform. When treated with excess of water, it is partly decomposed with the precipitation of red mercuric iodide. Concentrated sulphuric acid causes the liberation of iodine.

G. T. M.

New Synthesis in the Quinazoline Group. By MARSTON T. BOGERT and AUGUST H. GOTTHELF (*J. Amer. Chem. Soc.*, 1900, 22, 129—132).—By the action of acetonitrile on anthranilic acid, Mathews (Abstr., 1899, i, 57) obtained a crystalline product melting at 232° . The authors have identified this substance as the 2-methyl-4-keto-dihydroquinazoline first described by Weddige (Abstr., 1885, 661, and 1887, 1044), and have extended the reaction to the preparation of the corresponding 2-ethyl-, 2-phenyl-, 2-benzyl-, and 2-*p*-tolyl-derivatives. The three last will be described later.

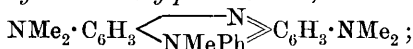
E. G.

Reactions in which Saffranines are formed. By D. HARDIN (*Ber.*, 1900, 33, 1212—1218).—A dilute neutral aqueous solution of *p*-diaminodiphenylamine sulphate (1 mol.) and the hydrochloride of a monamine (1 mol.) was heated with a little oxalic acid and oxidised with manganese dioxide. Under these circumstances the following amines yielded saffranines: Aniline, *o*-, *m*-, and *p*-toluidines, 1:2:4- and 1:3:4-xylidines, 2:4:5-trimethylaniline, 2:3:4:5- and 2:3:4:6-tetramethylanilines, and pentamethylaniline. 1:2:3-, 1:4:3-, 1:3:2-, and 1:3:5-Xylidines, 2:4:6-, 3:4:5-, 2:3:4- (?) and 2:3:5-trimethylanilines, and 2:3:5:6-tetramethylaniline do not form saffranines under the same conditions. From this it appears that a saffranine is formed when one methyl group is attached to the benzene nucleus of the amine, whatever the position of the group relatively to the amino-group; that when two or more methyl groups are present one must be in the para-position if a saffranine is to be formed, and that the rest must be in pairs occupying para-positions relatively to each other, the position of an odd one left over being indifferent.

In some cases, a saffranine is formed when *p*-phenylenediamine (1 mol.) and a monamine (2 mols.) are oxidised together. If an indamine is formed as a first stage in the production of the saffranine, it might be expected that the para-position in the amine ought not to be occupied, as in the opposite case the formation of an indamine is impossible. As a matter of fact, it was found that *m*-toluidine does form a saffranine with *p*-phenylenediamine and 1:2:4-xylidine does not. 1:3:2- and 1:4:3-Xylidines, however, yield an indamine, but no saffranine.

Nitrosodimethylaniline hydrochloride forms a saffranine when it is heated with a monamine (1 mol. of each) in alcoholic solution; and it might be thought that those amines which do not form a saffranine with *p*-phenylenediamine would form none with nitrosodimethylaniline. Although, however, *p*-toluidine does not form a saffranine, it is found that 1:3:2-, 1:4:3-, and 1:2:3-xylidines do so. Consequently the saffra-

nines are formed in this case without the intermediate formation of an indamine, and it is necessary for their formation that the para-position should not be occupied. From nitrosodimethylaniline and dimethylaniline a monacid base was obtained which is probably *B*₁-4-dimethylamino-*B*₂-4-dimethylaminomethylphenazonium,



its *mercurichloride* was analysed.

Suggestions are made as to the course of the reaction in which a saffranine is formed; for these, the original must be consulted.

C. F. B.

Action of Thiocyanacetic Acid on Phenylhydrazine. By CARL D. HARRIES and ERNST KLAMT (*Ber.*, 1900, 33, 1152—1160).—*Aniliminocarbaminothioglycollic acid*, $\text{NPh} \cdot \text{N} : \text{C}(\text{NH}_2) \cdot \text{S} \cdot \text{CH}_2 \cdot \text{CO}_2\text{H}$, prepared by the action of phenylhydrazine on thiocyanacetic acid (Claesson, *Abstr.*, 1878, 37), crystallises from boiling alcohol and melts at 149°; the substance has no marked basic properties and a nitroso-derivative could not be prepared. *Methylaniliminocarbaminothioglycollic acid*, $\text{NMePh} \cdot \text{N} : \text{C}(\text{NH}_2) \cdot \text{S} \cdot \text{CH}_2 \cdot \text{CO}_2\text{H}$, prepared by the action of *as*-phenylmethylhydrazine on thiocyanacetic acid, melts at 146° and resembles the preceding acid.

Phenylaminopyridothiazinone, $\text{CO} \left\langle \begin{array}{c} \text{NPh} \cdot \text{N} \\ \text{CH}_2 \cdot \text{S} \end{array} \right\rangle \text{C} \cdot \text{NH}_2$, prepared by heating aniliminocarbaminothioglycollic acid above its melting point, or by heating ethyl thiocyanacetate (Heintz, *Annalen*, 1865, 136, 223) with phenylhydrazine, crystallises from alcohol in colourless prisms and melts at 176°; the *hydrochloride* crystallises in needles and melts at 190°; the violet *potassium* salt crystallises in pearly prisms, and is regarded as derived from a hydroxylic modification of the base.

Phenyldiazopyridothiazinone, $\text{CO} \left\langle \begin{array}{c} \text{NPh} \cdot \text{N} \\ \text{CH}_2 \cdot \text{S} \end{array} \right\rangle \text{C} \cdot \text{N} : \text{N} \cdot \text{OH}$, prepared by the action of nitrous acid on the preceding compound, is a white, crystalline substance which blackens at 75° and melts with decomposition at 130°; it does not give Liebermann's reaction, and could not be converted into the thiazole by boiling with alcohol.

Diaminocarbiminothioglycollic acid, $\text{NH}_2 \cdot \text{N} : \text{C}(\text{NH}_2) \cdot \text{S} \cdot \text{CH}_2 \cdot \text{CO}_2\text{H}$, crystallises in white needles and melts at 92°. By boiling with water, it is converted into an *anhydride*, probably $\text{CO} \left\langle \begin{array}{c} \text{NH} \cdot \text{N} \\ \text{CH}_2 \cdot \text{S} \end{array} \right\rangle \text{C} \cdot \text{NH}_2$, which separates in white prisms and melts at 277°. T. M. L.

Action of Methyl Iodide on Dithiodiazolone Disulphides; Decomposition of Thiodiazolones. By MAX BUSCH and EDMUND LINGENBRINK (*J. pr. Chem.*, 1900, [ii], 61, 330—335).—Phenyldithiodiazolone disulphide (*Abstr.*, 1894, i, 625), on treatment with methyl iodide in alcoholic solution, yields phenylthiodiazolone methosulphide (E. Wolpert, *Inaug. Diss. Erlangen*, 1899, 35), which, when warmed with ethyl alcoholic potash, gives *methyl ethyl phenyldithiocarbazine α-carboxylate*, $\text{SH} \cdot \text{C}(\text{SMe}) : \text{N} \cdot \text{NPh} \cdot \text{CO}_2\text{Et}$, which crystallises in prisms

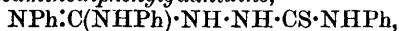
melting at 101° , and can also be prepared by the action of ethyl chlorocarbonate on methyl phenyldithiocarbazinate. The corresponding *methyl* compound, obtained when the methosulphide is decomposed by methyl alcoholic potash, crystallises in six-sided prisms melting at 114° . *p*-Tolythiodiazolone methosulphide (Wolpert, *loc. cit.*) is obtained in a similar manner from *p*-tolyldithiodiazolone disulphide, and on treatment with ethyl alcoholic potash yields *methyl ethyl p-tolyl-carbazinic- α -carboxylate*, which crystallises in silvery needles or prisms melting at 111° .
R. H. P.

Products of the Action of Hydrazine on Thiocarbamides. By MAX BUSCH and PAUL BAUER (*Ber.*, 1900, 33, 1058—1073).—Thiocarbanilide reacts with hydrazine hydrate in alcoholic solution, yielding 4-phenylsemicarbazide and aniline; in presence of alcoholic potash, however, potassium hydrosulphide and a substituted aminoguanidine are produced.

Aminodiphenylguanidine, $\text{NPh}\cdot\text{C}(\text{NHPh})\cdot\text{NH}\cdot\text{NH}_2$, is obtained by heating thiocarbanilide with a large excess of hydrazine hydrate and alcoholic potash in closed tubes at 110 — 115° , but is accompanied by large quantities of its aniline-additive product, diphenylcarbamide, and a basic substance melting at 232° . It separates from a mixture of ether and light petroleum in crusts of compact crystals, sinters at 96° , melts at 98 — 99° , decomposes at 180° , and is somewhat readily soluble in the common media with the exception of light petroleum and water. From benzene, crystals having the composition $\text{C}_{13}\text{H}_{14}\text{N}_4\cdot\text{C}_6\text{H}_6$ are obtained. It combines with aniline to form a substance, $\text{C}_{13}\text{H}_{14}\text{N}_4\cdot\text{C}_6\text{H}_7\text{N}$, whose properties have already been described (this vol., i, 27); the corresponding compound, with *p*-toluidine, $\text{C}_{13}\text{H}_{14}\text{N}_4\cdot\text{C}_7\text{H}_9\text{N}$, crystallises in white needles and melts at 108° . It does not combine with α - or β -naphthylamine. *Aminodiphenylguanidine nitrate*, $\text{C}_{13}\text{H}_{14}\text{N}_4\cdot\text{HNO}_3$, forms quadratic tables, and melts at 184 — 186° . The *sulphate* melts indefinitely at 95° . The *hydrochloride* forms slender, white needles. The *picrate* is deposited from ether in yellow leaflets containing $\frac{1}{2}$ mol. of the solvent and melting at 135° . The *oxalate* forms leaflets and melts and decomposes at 209 — 210° .

Benzylidenaminodiphenylguanidine, $\text{NPh}\cdot\text{C}(\text{NHPh})\cdot\text{NH}\cdot\text{N}\cdot\text{CHPh}$, dissolves readily in the usual media, crystallises from dilute alcohol in yellowish needles, and melts at 121 — 122° . The *nitrate* forms lustrous, transparent, compact needles, and melts at 157° . The *m-nitro*-derivative forms intensely yellow, lustrous needles, melts at about 130° , and is readily soluble in ether or benzene.

Thiocarbanilinoaminodiphenylguanidine,



forms silky needles melting at 137° , and separates from benzene in snow-white needles which contain the solvent and melt at about 90° .

5-*Anilino-4-phenyltriazole*, $\text{N}\begin{smallmatrix} \text{N}=\text{CH} \\ \text{C}(\text{NHPh}) \end{smallmatrix}\text{NPh}$, prepared by heating aminodiphenylguanidine with formic acid, separates from alcohol in long, slender, silky needles, melts at 213° , has markedly basic properties, and dissolves readily in boiling alcohol, chloroform,

or dilute mineral acids, but does not form a stable acetate. It is not affected by nitrous acid or by concentrated hydrochloric acid at 220°, but is suddenly decomposed at higher temperatures. The *acetyl* derivative, $C_{14}H_{11}N_4Ac$, melts at 170—171°.

5-Anilino-4-phenyl-3-methyltriazole, $N \begin{smallmatrix} \diagup N=CMe \\ \diagdown C(NHPh) \end{smallmatrix} > NPh$, from aminodiphenylguanidine and acetic anhydride, is readily soluble in alcohol; it separates from benzene in lustrous, flat needles or leaflets melting at 227—228°. The *hydrochloride*, $C_{15}H_{14}N_4 \cdot HCl$, forms white needles.

*Benzoylamino*diphenylguanidine, $NPh \cdot C(NHPh) \cdot NH \cdot NHBz$, separates from alcohol in beautiful transparent needles which melt with effervescence at 173°; it dissolves in mineral acids and forms a sparingly soluble *sulphate*, which forms needles melting at 221—222°.

5-Anilino-3:4-diphenyltriazole, $N \begin{smallmatrix} \diagup N=CPh \\ \diagdown C(NHPh) \end{smallmatrix} > NPh$, formed when the foregoing substance is heated above its melting point, separates from alcohol in large, transparent prisms, dissolves readily in acetic acid and chloroform, and melts at 210—211°; the *hydrochloride*, $C_{20}H_{16}N_4 \cdot HCl$, forms white needles melting at 220—223°, and is dissociated in water.

Phenyliminophenyltetrazolone, $\begin{smallmatrix} N \cdot NPh \\ || \\ N-NH \end{smallmatrix} > C:NPh$, prepared from aminodiphenylguanidine by the action of nitrous acid, separates from alcohol in shining, slender needles, melts at 162—163° and decomposes at 220°, is readily soluble in warm alcohol, benzene, or chloroform, and has feebly acid properties, forming salts with alkalis which are decomposed by water. The *acetyl* derivative, $C_{15}H_{13}ON_5$, separates from dilute alcohol in transparent, compact crystals and melts at 85—89°.

Aminodi-o-tolylguanidine, $C_7H_7N:C(NH \cdot C_7H_7) \cdot NH \cdot NH_2$, prepared from di-o-tolylthiocarbamide and hydrazine, separates from alcohol in shining needles melting at 120°, and dissolves readily in the ordinary media, with the exception of petroleum. The *nitrate*, melting at 118—119°, and the *sulphate* are described.

Benzylidenaminodi-o-tolylguanidine,
 $C_7H_7 \cdot N:C(NH \cdot C_7H_7) \cdot NH \cdot N:CHPh$,
 crystallises from alcohol in aggregates of yellowish needles melting at 125—126°.

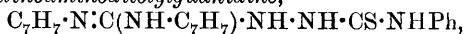
5-o-Toluidino-4-o-tolyl-3-methyltriazole, $C_7H_7 \cdot N \begin{smallmatrix} \diagup N=CMe \\ \diagdown C(NH \cdot C_7H_7) \end{smallmatrix} > N$, prepared from aminoditolylguanidine and acetic anhydride, crystallises from benzene in small, lustrous prisms and melts indefinitely at 172—175°.

o-Tolylimino-o-tolyltetrazolone, $N \begin{smallmatrix} \diagup N(C_7H_7) \\ \diagdown N-NH \end{smallmatrix} > C:N \cdot C_7H_7$, forms white, shining needles and melts at 152°.

Aminodi-p-tolylguanidine crystallises from alcohol in beautiful, transparent prisms melting at 152°. The *benzylidene* derivative forms needles melting at 123—124° and is readily hydrolysed by acids. The *o-hydroxybenzylidene* compound, $C_{15}H_{16}N_4 \cdot CH \cdot C_6H_4 \cdot OH$, forms

yellowish needles and dissolves in alcoholic soda, forming an intensely yellow solution which, in presence of excess of alkali, deposits the sodium derivative in yellow leaflets.

Thiocarbanilinoaminoditolylguanidine,



forms white, silky leaflets melting at 148°.

5-p-Toluidino-4-p-tolyltriazole, $\text{C}_7\text{H}_7\text{---N}\cdot\text{CH} \begin{smallmatrix} \nearrow \\ \searrow \end{smallmatrix} \text{N} \begin{smallmatrix} \nearrow \\ \searrow \end{smallmatrix} \text{N} \begin{smallmatrix} \nearrow \\ \searrow \end{smallmatrix} \text{N} \begin{smallmatrix} \nearrow \\ \searrow \end{smallmatrix} \text{CH} \cdot \text{NHPH}$, prepared from aminoditolylguanidine and formic acid, crystallises in colourless leaflets melting at 224.

p-Tolylimino-p-tolyltetrazolone crystallises in silky, slender, felted needles and melts at 207°. A. L.

A New Synthesis of Guanine and of Xanthine. By WILHELM TRAUBE (*Ber.*, 1900, 33, 1371—1383. Compare E. Fischer, *Abstr.*, 1898, i, 48).—A mixture of *cyanoacetylguanidine*, $\text{NH}:\text{C}(\text{NH}_2)\cdot\text{NH}\cdot\text{CO}\cdot\text{CH}_2\cdot\text{CN}$, and of *2:4-diamino-6-hydroxypyrimidine*, $\text{NH}_2\cdot\text{C} \begin{smallmatrix} \nearrow \\ \searrow \end{smallmatrix} \text{CH}\cdot\text{C}(\text{OH}) \begin{smallmatrix} \nearrow \\ \searrow \end{smallmatrix} \text{N}:\text{C}(\text{NH}_2) \begin{smallmatrix} \nearrow \\ \searrow \end{smallmatrix} \text{N}$, is obtained by the action of sodium ethoxide and ethyl cyanoacetate on guanidine hydrochloride; the former crystallises out as the solution cools, and the pyrimidine derivative may be obtained on evaporating the mother liquor; neither compound has a definite melting point. The guanidine compound is readily converted into the isomeric diaminohydroxypyrimidine when warmed with hot dilute sodium hydroxide, and on the addition of dilute sulphuric acid the pyrimidine *sulphate*, $(\text{C}_4\text{H}_6\text{ON}_4)_2\cdot\text{H}_2\text{SO}_4\cdot\text{H}_2\text{O}$, crystallises out; the corresponding nitrate and hydrochloride are readily soluble. Sodium nitrite reacts with an aqueous solution of the sulphate, yielding a *nitroso-derivative*, $\text{C}_4\text{H}_5\text{O}_2\text{N}_5$; this crystallises in small, rose-coloured needles, is sparingly soluble in the usual solvents, and possesses neither basic nor acidic properties. When reduced with ammonium sulphide, it yields *2:4:5-triamino-6-hydroxypyrimidine*, a diacid base which separates from water in practically colourless crystals; the *sulphate*, $\text{C}_4\text{H}_7\text{ON}_5\cdot\text{H}_2\text{SO}_4\cdot\text{H}_2\text{O}$, crystallises in small, colourless needles, and when heated with the equivalent amount of sodium formate, and 8—10 times its weight of anhydrous formic acid yields guanine, which, in its turn, can be converted into xanthine by Fischer's method.

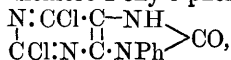
Cyanoacetylcarbamide (compare Mulder, *Abstr.*, 1879, 619) is best obtained by the action of carbamide on a mixture of cyanoacetic acid and phosphorus oxychloride; it crystallises from water in colourless crystals, and melts at 209°, and when treated with sodium hydroxide, and then with acetic acid, yields *4-amino-2:6-dihydroxypyrimidine*; this crystallises from water, has no definite melting point, and possesses both basic and acidic properties; when treated with nitrous acid, it yields an isonitroso-compound which, on reduction, gives *4:5-diamino-2:6-dihydroxypyrimidine*, the *sulphate* of which, $(\text{C}_4\text{H}_6\text{O}_2\text{N}_4)_2\cdot\text{H}_2\text{SO}_4\cdot 1\frac{1}{2}\text{H}_2\text{O}$, is sparingly soluble in water. When boiled with formic acid (90 per cent.), it is converted into the *formyl derivative*, $\text{C}_6\text{H}_6\text{O}_3\text{N}_4\cdot\frac{1}{2}\text{H}_2\text{O}$, which becomes anhydrous at 150°.

J. J. S.

Aromatic Derivatives of Uric Acid. By EMIL FISCHER (*Chem. Centr.*, 1900, i, 806—807; from *Sitzungsber. Akad. Wiss. Berlin*, 1900, 122—130).—By the action of phenyl cyanate in alkaline solution on uramil under conditions similar to those described by Paal (*Ber.*, 27, 974), γ -phenyl- ψ -uric acid, $\begin{array}{c} \text{NH}\cdot\text{CO}\cdot\text{C}\cdot\text{NH}\cdot\text{CO}\cdot\text{NHPh} \\ | \quad | \\ \text{CO}\cdot\text{NH}\cdot\text{CO} \end{array}$, is formed.

This acid crystallises from 350 parts of water in aggregates of small needles; at 120°, it still retains $\frac{1}{2}\text{H}_2\text{O}$; it chars at a higher temperature. It is almost insoluble in alcohol or ether, reduces ammoniacal silver solutions, and gives the murexide reaction. Carbon dioxide precipitates acid salts from alkaline solutions of the acid. The potassium, sodium, and ammonium salts are only slightly soluble in water, the potassium being less soluble than the sodium salt.

3-Phenyluric acid, $\begin{array}{c} \text{NH}\cdot\text{CO}\cdot\text{C}\cdot\text{NH} \\ | \quad | \\ \text{CO}\cdot\text{NH}\cdot\text{C}\cdot\text{NPh} \end{array} > \text{CO}$, prepared by boiling the pseudo-acid with dilute hydrochloric acid, crystallises from water with $2\text{H}_2\text{O}$, forming lustrous, silvery leaflets, or very small, thin, rectangular plates. At 320°, the acid becomes brown and chars at a higher temperature; it is more soluble in water than the corresponding methyluric acid, dissolving in about 120 parts of boiling water, and is very slightly soluble in alcohol. The potassium salt forms small prisms or plates, and the acid salt, $\text{C}_{11}\text{H}_7\text{O}_3\text{N}_4\text{K}$, spherical aggregates of needles. The ammonium salt also crystallises in aggregates of small needles. 3-Phenyluric acid reduces ammoniacal silver solutions, is easily attacked by potassium permanganate or nitric acid, and by the action of chlorine forms alloxan and a crystalline compound which is probably a chloro-derivative of phenylcarbamide. By heating the acid with fuming hydrochloric acid at 170°, glycocine, ammonium chloride, and aniline are formed, and by the action of phosphorus oxychloride at 170°, 5 : 7-dichloro-2-oxy-3-phenylpurine,



is obtained, together with a compound which is insoluble in alkalis, and is probably phenyltrichloropurine. Phenoxydichloropurine crystallises from glacial acetic acid in small, flexible needles, melts at 323° (corr.), and distils in small quantities almost without decomposition; it is slightly soluble in hot water, almost insoluble in ether or in concentrated hydrochloric acid, but dissolves easily in concentrated sulphuric acid at 100° without undergoing any change. The alkali salts crystallise in needles, and are easily soluble in hot water, but only slightly so in alkalis. The ammonium salt crystallises in pointed prisms or plates. Phenoxydichloropurine dissolves in considerable quantities in cold hydriodic acid of sp. gr. 1.96, and on warming, with or without the addition of phosphonium iodide, a compound which contains iodine and is easily soluble in alkalis, separates out.

3-Phenyl-1 : 4 : 6-trimethyluric acid, $\begin{array}{c} \text{NMe}\cdot\text{CO}\cdot\text{C}\cdot\text{NMe} \\ | \quad | \\ \text{CO}\cdot\text{NMe}\cdot\text{C}\cdot\text{NPh} \end{array} > \text{CO}$, prepared by shaking an alkaline solution of phenyluric acid with methyl iodide at 85°, crystallises in rhomb-like plates, melts at 265—266° (corr.), distils with slight decomposition at a higher temperature, is

soluble in about 30 parts of boiling alcohol, and is not attacked by cold alkalis, but dissolves on boiling, being decomposed in a similar manner to tetramethyluric acid.

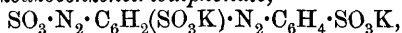
The aminophenols also act on phenyl cyanate in alkaline solution. The *phenyl carbamate* of *p*-hydroxydiphenylcarbamide, $\text{NHPh}\cdot\text{CO}\cdot\text{O}\cdot\text{C}_6\text{H}_4\cdot\text{NH}\cdot\text{CO}\cdot\text{NHPh}$, prepared from *p*-aminophenol, crystallises from about 100 parts of glacial acetic acid; it sinters at 220° , melts and decomposes at 240° , and is dissolved by prolonged boiling with alkali, being partially converted into *p*-hydroxydiphenylcarbamide, $\text{HO}\cdot\text{C}_6\text{H}_4\cdot\text{NH}\cdot\text{CO}\cdot\text{NHPh}$, which is precipitated from the alkaline solution by acids, and separates from glacial acetic acid in spherical aggregates of needles, melts at 221° (corr.), is slightly soluble in hot water, ether, or benzene, and closely resembles Leuckart's isomeric ortho-compound.

E. W. W.

Aminoazobenzenetrisulphonic Acid. By ALFRED JUNGHAHN and MAX NEUMANN (*Ber.*, 1900, 33, 1366—1371).—4'-Aminoazobenzene-4 : 3' : 5'-trisulphonic acid, $\text{SO}_3\text{H}\cdot\text{C}_6\text{H}_4\cdot\text{N}_2\cdot\text{C}_6\text{H}_2(\text{SO}_3\text{H})_2\cdot\text{NH}_2$, is formed when aminoazobenzene hydrochloride is brought rapidly into fuming sulphuric acid and the mixture heated; it is much more readily soluble than the disulphonic acid, which is also formed, whilst its *potassium* salt is less soluble than that of the disulphonic acid. The acid is also formed by the sulphonation of the disulphonic acid, and crystallises in small plates, which have a silvery lustre; on reduction, it yields sulphanilic acid and a *p*-phenylenediaminedisulphonic acid, $\text{C}_6\text{H}_2(\text{NH}_2)_2(\text{SO}_3\text{H})_2[\text{NH}_2:\text{NH}_2:\text{SO}_3\text{H}:\text{SO}_3\text{H} = 1:4:2:6]$, which crystallises in white plates. Nitric acid converts this compound into picric acid, its constitution, and that of the trisulphonic acid, being thus proved.

The *dipotassium hydrogen* salt of aminoazobenzenetrisulphonic acid is precipitated when the normal salt is treated with hydrochloric acid, and crystallises in large, dark blue plates. The normal *barium* salt crystallises in yellow needles, and the *barium hydrogen* salt in steel, blue plates, whilst the *normal ammonium* salt crystallises in yellow plates.

Potassium diazoazobenzenetrisulphonate,



is formed when the normal potassium salt of the trisulphonic acid is diazotised, and crystallises in brown needles which decompose in the air; when boiled with alcohol, nitrogen is evolved, and *potassium hydrogen azobenzenetrisulphonate* is produced, which, however, could not be obtained pure. The trisulphonic acid itself dyes silk and wool a fast yellow; the azo-dyes formed with phenol, β -naphthol, and *p*-tolyl- β -naphthylamine are very similar to those derived from aniline-yellow, but the shades are more yellowish or brownish.

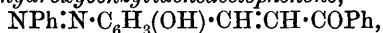
A. H.

Constitution of Hydroxyazo-compounds. By KARL AUWERS [and G. MANN] (*Ber.*, 1900, 33, 1302—1315. Compare Abstr., 1897, i, 40).—The results of a cryoscopic examination of phenylhydrazones in *p*-dibromobenzene are tabulated. From these it is possible to formulate rules to decide from the cryoscopic behaviour of *p*-hydroxyazo-compounds in the same solvent whether they are quinone-hydrazones or

phenols. The determinations clearly show that they are phenols. This result is not in accordance with Hantzsch's views (Abstr., 1899, i, 400), but agrees with the chemical behaviour of these substances (compare Hewitt, Trans., 1900, 77, 99 and 712). R. H. P.

Benzeneazosalicylaldehyde. By WALTHER BORSCHKE (*Ber.*, 1900, 33, 1325—1328).—Benzeneazosalicylaldehyde can readily be prepared from hydroxyazobenzene and chloroform. The compound with aniline crystallises in brown needles melting at 135—136°.

3-Benzeneazo-6-hydroxybenzylideneacetophenone,



is formed by the action of benzeneazosalicylaldehyde on acetophenone and crystallises in orange-red nodules which melt and decompose at 187—188°. The sodium compound forms garnet-red plates, with a green lustre. The same substance is also formed, but in small quantity, by the reaction of *o*-hydroxybenzylideneacetophenone on diazobenzene chloride. A. H.

Sulphur Derivatives from *p*-Aminophenol and Hydroxyazobenzene. By CRISTOPH RIS (*Ber.*, 1900, 33, 796—799).—*p*-Aminophenol (4 mols.), hydroxyazobenzene (2 mols.), and sulphur (7 at.) are melted in a porcelain beaker and kept well-stirred at a temperature of 180—190°, when ammonia and aniline are evolved; the fused mass is boiled with dilute hydrochloric acid, when a black dye remains undissolved, and, on the addition of sodium acetate to the acid filtrate, a greenish-white precipitate is deposited. This contains both nitrogen and sulphur (N = 8·56, S = 26·37 per cent.); it rapidly darkens when dried, even at low temperatures, possesses both basic and acidic properties, and dissolves in alcohol to a pale yellowish-grey solution, which, however, on exposure to the air, gradually deposits a thick, black precipitate. When treated with reducing agents, much hydrogen sulphide is evolved, and a product very similar to the original substance is produced; oxidising agents, on the other hand, give rise to a heavy, black dye which dissolves in alkalis to a black solution. A black dye is also formed when the original compound is heated with a further quantity of sulphur.

m-Amino-*o*-cresol, or *p*-phenylenediamine, may be employed instead of *p*-aminophenol and other hydroxyazo-compounds in place of hydroxyazobenzene. *p*-Aminophenol itself, when heated with sulphur, gives rise to a substance which is deposited as a greyish-white precipitate on the addition of sodium acetate solution to the hydrochloric acid extract of the fused mass. On oxidation, it yields a purple-black precipitate, and its ammonium sulphide solution, on exposure to the air, assumes a clear blue colour. It contains nitrogen 8·25, and sulphur 23·09 per cent., and is not leucothionol. J. J. S.

Digestion of Fibrin and Albumin by Papain. By V. HARLAY (*J. Pharm.*, 1900, [vi], 11, 172—178. Compare Abstr., 1899, i, 835).—Papain, in the form of the diluted latex of *Carica hastifolia*, rapidly digests fibrin at 45—50°, and the action is only slightly retarded by rendering the solution feebly alkaline by sodium hydrogen carbonate, although boiling, or the presence of 0·34 per cent. of hydrochloric acid

totally prevents it. The liquid from the digestion gives with *Russula delica* a colour change of red to green, resembling that obtained similarly in the peptic digestion of fibrin (*loc. cit.*) ; the final green obtained in the former case, however, has a slightly bluer shade. Little tyrosine, if any, appears to be formed, so that the digestion of fibrin by papain is markedly different from that effected by pancreatic juice.

The papain digestion of albumin is very similar to that effected by pepsin, although *Russula delica* produces with the former a dark green solution having a characteristic absorption band in the orange of the spectrum, whereas in the case of pepsin this is absent ; the solution, moreover, is dichroic, appearing green in transmitted, red in reflected light. With solutions obtained by peptic digestion, however, the same absorption band is observed after reduction with zinc and hydrochloric acid.

W. A. D.

Action of Heat on Papain. By V. HARLAY (*J. Pharm.*, 1900, [vi], 11, 268—272).—The digestive action of papain on fibrin is not changed by heating the dry enzyme for 3 hours at 100°, but in aqueous solution heat rapidly destroys the ferment ; at 82·5°, the destruction is complete in 30 minutes, whilst at lower temperatures it takes place more slowly.

W. A. D.

Yeast Extract and Precipitating Agents. By ROBERT ALBERT and EDUARD BUCHNER (*Ber.*, 1900, 33, 971—975. Compare this vol., i, 329).—When fresh yeast extract is poured into a mixture of alcohol and ether, a precipitate is obtained which after drying has not lost its fermenting properties. This precipitate is not completely soluble in water, but the turbid liquid obtained possesses strong fermenting properties which are, however, greatly diminished when it is filtered. The dried precipitate is more readily soluble in glycerol, and the solution, after filtration, ferments just as readily as before ; when the glycerol solution is poured into alcohol and ether, a precipitate is obtained which is also capable of inducing fermentation. It has been shown by experiment that yeast extract which has been allowed to remain in contact with 10 per cent. glycerol for some 20 hours at the ordinary temperature ferments more readily than the same extract which has been kept for the same length of time without the addition of glycerol. This is probably due to the fact that the addition of glycerol hinders, to a certain extent, the action of proteolytic enzymes in the extract which tend to destroy the zymase.

J. J. S.

Organic Chemistry.

Configuration of Saturated Fatty Compounds. By PAVEL IW. PETRENKO-KRITSCHENKO (*J. pr. Chem.*, 1900, [ii], 61, 431—439).—The author opposes Krafft's view that in saturated fatty compounds the favoured configuration is the one which approximates to that of the corresponding polymethylene compounds. In the oxalic series, the dissociation constant steadily decreases as the molecular weight increases, suggesting that the two carboxyl groups are furthest apart and influence each other least in the higher homologues and do not tend to approach each other as they should do according to Krafft's hypothesis. In a number of other cases, it is pointed out that polymethylene compounds do not resemble the open-chain derivatives containing the same number of carbon atoms, but rather the corresponding dimethyl compounds; thus hexamethyleneamine resembles isopropylamine rather than the higher homologues, and ketopentamethylene and other cyclo-ketones resemble acetone in forming compounds with sodium hydrogen sulphite. T. M. L.

Hydrogenation of Acetylene in Presence of Copper. By PAUL SABATIER and JEAN BAPTISTE SENDERENS (*Compt. rend.*, 1900, 130, 1559—1561. Compare Abstr., 1899, i, 555).—When a mixture of acetylene and hydrogen, containing excess of the latter, is passed over finely-divided reduced copper at 200°, the resultant gas contains about 3 per cent. of olefines and 18 per cent. of ethane; with more compact copper at 170°, the percentage of olefine is increased nine-fold, whilst that of ethane is diminished by one-third. When the mixture contains half its volume of acetylene, the reaction sets in at 150°, and is attended by the formation of cuprene (this vol., i, 197); the yield of ethylene and its higher homologues is even greater than in the preceding experiments, whilst that of ethane falls to 2 per cent.

G. T. M.

Addition of Hypochlorous and Hypobromous Acids to Acetylene and to its Mono-substituted Derivatives. By NICOLAUS M. WITTORFF (*J. Russ. Phys. Chem. Soc.*, 1900, 32, 88—117).—The action of hypobromous acid on acetylene yields a small quantity of dibromoacetic acid, the chief product, however, being dibromoacetaldehyde, of which a new *hydrate*, $C_2H_2OBr_2 \cdot 2H_2O$, melting at 40—60°, was obtained. The action of hydroxylamine on this compound gives rise to glyoxime.

With allylene, hypobromous acid yields unsymmetrical dibromoacetone, which, by the action of hydroxylamine, is converted into methylglyoxime.

Trimethylallylene, $CH_3C \cdot CMe_3$, and hypobromous acid react together with the formation of a dibromopinacolin identical with the compound obtained by Scholl and Weil (*Chem. Zeit.*, 1899, 23, 189) by the action of bromine on pinacolin, and by Kondakoff (Abstr., 1899, i, 859) by treating pinacone with concentrated hydrobromic acid; the latter regarded it as having the constitution $CH_2Br \cdot CO \cdot CMe_2 \cdot CH_2Br$. The

authors find, however, that when heated in alcoholic solution with hydroxylamine hydrochloride and potassium hydroxide, it is converted into a dioxime, $C_6H_{12}O_2N_2$; also when heated with 10 per cent. potassium hydroxide solution it yields trimethylactic acid, $CMe_3 \cdot CH(OH) \cdot CO_2H$. The compound must hence be α -dibromopinacolin, $CMe_3 \cdot CO \cdot CHBr_2$, the dioxime formed from it having the constitution $CMe_3 \cdot C(NO_2) \cdot CH \cdot NO_2$; the latter crystallises from dilute alcohol in oblique prisms melting at $101-102^\circ$.

Hypobromous acid combines with phenylacetylene, giving dibromoacetophenone, $CHBr_2 \cdot CPh$, and a small quantity of a bromide probably identical with the compound obtained by Schramm (Abstr., 1885, 518) by brominating ethylbenzene in sunlight, to which the constitution $CMePhBr_2$ was assigned. When treated with hydroxylamine, dibromoacetophenone yields phenylglyoxime.

Hypochlorous acid acts on acetylene and its mono-substituted derivatives in a manner analogous to that of hypobromous acid, the dichloroketones obtained yielding with hydroxylamine the same dioximes as the corresponding dibromo-compounds. Thus, with acetylene, the initial product of the reaction, which must be carried out at a low temperature and in presence of excess of hypochlorous acid, is dichloroacetaldehyde, most of which, however, undergoes oxidation to dichloroacetic acid. With allylene, *as*-dichloroacetone and a small quantity of methylglyoxal are formed. Trimethylallylene gives rise to the α -dichloropinacolin, $CMe_3 \cdot CO \cdot CHCl_2$, obtained by Fittig by the direct chlorination of pinacolin; with 10 per cent. potassium hydroxide solution, this compound yields trimethylactic acid. With phenylacetylene, hypochlorous acid gives α -dichloroacetophenone, $CHCl_2 \cdot CPh$, melting at $20-21.5^\circ$.
T. H. P.

Hydrocarbon C_6H_{10} from Dimethylallylcarbinol. By EUGÈNE LUBARSKY (*J. Russ. Phys. Chem. Soc.*, 1900, 32, 140-149).—The author has investigated the hydrocarbon C_6H_{10} obtained by Saytzeff (this Journal, 1877, ii, 298). It is prepared by treating dimethylallylcarbinol with hydrogen chloride in the cold, the chloride thus obtained being treated with alcoholic potash to remove hydrogen chloride. On fractionating the product in an atmosphere of carbon dioxide, the hydrocarbon is obtained as a colourless, mobile liquid boiling at $73-76^\circ$; it has a characteristic hydrocarbon odour recalling that of kerosene, and shows slight violet-blue fluorescence. It has a sp. gr. 0.71427 at $20^\circ/0^\circ$; 0.71504 at $20^\circ/20^\circ$; 0.71415 at $20^\circ/4^\circ$. At 20° , it has the refractive indices μ_a 1.43840 , μ_β 1.45450 , the value for infinite wave-length being hence 1.41888 ; the molecular refraction (Perkin's formula) for the ray of infinite wave-length is 48.09 , the value calculated from the composition of the hydrocarbon, and allowing for the presence of two double bonds, being 42.06 ; this difference is probably due to oxidation of the compound, as it absorbs oxygen readily from the air, giving a thick, slightly sticky, yellowish oil. On treating the hydrocarbon with hypochlorous acid, and acting on the additive compound thus obtained with an ethereal solution of potassium hydroxide, hydrogen chloride is removed and a compound formed having the composition $C_6H_{10}O(OH)_2$, and the probable constitution

$\text{CH}_2 \begin{matrix} \text{CMe(OH)·CH}_2 \\ \text{CH(OH)—CH}_2 \end{matrix} > \text{O}$. The hydrocarbon C_6H_{10} is hence probably *αα*-methylallylethylene, $\text{CH}_2\text{:CH·CH}_2\text{·CMe:CH}_2$. T. H. P.

Action of Zinc Dust on Trimethylene Bromide. By ALESEI A. WOLKOFF and BORIS N. MENSCHUTKIN (*J. Russ. Phys. Chem. Soc.*, 1900, 32, 118—139. Compare Abstr., 1899, i, 196).—The results obtained by Gustavson (Abstr., 1899, i, 421) and Tanatar (Abstr., 1899, i, 422) are criticised, and further experiments described, which lead to the following conclusions. Pure trimethylene cannot be obtained by the action of zinc dust and water on trimethylene bromide, or by the action of sodium on a xylene solution of trimethylene bromide; in both cases, the gas formed contains propane, and possibly hydrogen. The occurrence of propylene in the gas obtained by the action of zinc dust and alcohol on trimethylene bromide is due to the presence in the zinc dust of zinc oxide, which gives rise to ethyl *α*-bromopropyl ether (*loc. cit.*), the latter being reduced by alcohol and zinc dust to propylene. The propane present is formed by the reduction of propyl bromide, itself formed by incomplete reduction of the trimethylene bromide. The action of bromine on the gas obtained from zinc dust and alcoholic solution of trimethylene bromide is as follows. The propane gives propyl or *isopropyl* bromide, which, by the further action of bromine, is almost completely converted into propylene bromide; the latter product is also formed from the propylene, whilst the trimethylene gives trimethylene bromide. Absorption by bromine cannot be used as a means of obtaining pure trimethylene, since, although the propylene is very quickly absorbed, the propane is taken up less quickly than is the trimethylene. T. H. P.

Glycol Monoiodohydrin. By ERNEST CHARON and PAIX-SÉAILLES (*Compt. rend.*, 1900, 130, 1407—1410).—When glycol monoiodohydrin is treated with aqueous potash, it yields ethylene oxide and a resinous product resembling aldol resin, but when gently heated with dry lead hydroxide, it yields acetaldehyde and lead iodide almost quantitatively.

In Buttleroff and Ossokin's experiments on the action of zinc methyl on the iodohydrin (*Annalen*, 1873, 165, 257), it is probable that vinyl alcohol was first formed, and changed at once into acetaldehyde, which, with the excess of zinc methyl, produced an alcohol that was in reality secondary, and not primary, as those observers supposed. In Meyer and Demuth's experiments with silver nitrite (*ibid.*, 1890, 256, 29), there was simple substitution, and the acetic acid observed by Henry was probably the result of a secondary action.

With ammonia, aniline, phenylhydrazine, and hydroxylamine, the iodohydrin yields the iodides of complex bases, which are being investigated.

The iodohydrin loses the elements of the halogen acid much more readily than chlorohydrin; the latter has no action on lead hydroxide.

C. H. B.

Partial Synthesis of *l*-Erythritol. By LÉON MAQUENNE (*Compt. rend.*, 1900, 130, 1402—1404).—*Acetylxylic nitrile*, which forms white or yellowish plates melting at $81\cdot5^\circ$, is obtained by

i i 2

the action of acetic anhydride and sodium acetate on the seemingly non-crystallisable xyloseoxime prepared by the action of hydroxylamine on xylose. *l-Erythroacetamide* is obtained from this nitrile by simply dissolving in a large excess of ammonia solution, and crystallises in colourless prisms which melt at 166° and are very soluble in cold water, although non-deliquescent. In order to obtain *l-erythritol*, the acetamide is hydrolysed, the erythrose reduced with sodium amalgam, and the erythritol separated in the form of benzoic acetal, from which it is isolated by hydrolysis. *l-Erythritol* crystallises from alcohol in slender, brilliant needles, and from water in bulky prisms, which melt at 88° ; its rotatory power in a 6 per cent. aqueous solution is $[\alpha]_D + 4.3^{\circ}$, but in a 1.5 per cent. alcoholic solution $[\alpha]_D - 15^{\circ}$. Its molecular weight, determined by the cryometric method, is 121, and, except for the sign of the rotation, it is identical with the product obtained by Bertrand by the hydrogenation of erythrulose or erythroketo (this vol., i, 377).

C. H. B.

Reduction of Erythrulose and Preparation of a New Erythritol; *d-Erythritol*. By GABRIEL BERTRAND (*Compt. rend.*, 1900, 130, 1472—1475. Compare this vol., i, 377).—*d-Erythritol* is obtained, together with the inactive modification, by reducing an acid solution of erythrulose with sodium amalgam. A crystal of the inactive compound is added to the syrupy product of reduction in order to induce the crystallisation of this modification, the mother liquor being then treated with benzaldehyde, and the *d-erythritol* isolated in the form of its benzylidene compound; the latter is hydrolysed with dilute sulphuric acid, the regenerated erythritol allowed to solidify, and then recrystallised from alcohol. It crystallises from water in rhombohedral prisms, melts at $88-89^{\circ}$, and has $[\alpha]_D - 4.46^{\circ}$. This substance is the optical antipode of the *l-erythritol* recently obtained by Maquenne from *l-xylose* (preceding abstract), and since it is derived from erythrulose it follows that this sugar is also a member of the *d-series*.

G. T. M.

Behaviour of Uranyl Acetate and some of its Double Salts towards Water. By JOSEF ZEHENTER (*Monatsh.*, 1900, 21, 235—255).—Uranyl acetate, $\text{UO}_2(\text{C}_2\text{H}_3\text{O}_2)_2 \cdot 2\text{H}_2\text{O}$, loses its water of crystallisation at 110° , and decomposes at 275° , leaving a residue of uranium trioxide (compare Wertheim, *J. pr. Chem.*, 1843, 29, 207). It has a sp. gr. 2.893 at 15° in benzene, and at the same temperature 7.694 parts dissolve in 100 parts of water. An aqueous solution remains unchanged in subdued light, but direct sunlight causes the separation of an unstable violet hydroxide (compare Zimmermann, *Annalen*, 216, 10, and Ebelmen, *J. pr. Chem.*, 1842, 27, 385). From a saturated solution of uranyl acetate, kept in twilight and constantly shaken, a *basic acetate*, $\text{UO}_2(\text{C}_2\text{H}_3\text{O}_2)_2 \cdot \text{UO}_2(\text{OH})_2 \cdot 3\frac{1}{2}\text{H}_2\text{O}$, slowly separates, which is soluble in acids, insoluble in alcohol, and is coloured dark yellow by potash solution. A second *basic acetate*, $\text{UO}_2(\text{C}_2\text{H}_3\text{O}_2)_2 \cdot 2\text{UO}_2(\text{OH})_2$, soluble in acids, is obtained as a sulphur-yellow powder when aqueous solutions are heated.

Potassium uranyl acetate, $\text{UO}_2(\text{C}_2\text{H}_3\text{O}_2)_2 \cdot \text{K}_2\text{C}_2\text{H}_3\text{O}_2 \cdot \frac{1}{2}\text{H}_2\text{O}$ (compare Wertheim, *loc. cit.*, and Rammelsberg, *Sitzb. preuss. Akad. Wiss.*, 1884,

2, 857), has a sp. gr. 2.396 at 15° in benzene. In 1 per cent. solution, it is not affected by light, but when heated, potassium hexauranate, $K_2O, 6UO_3, 10H_2O$, separates as a yellow powder soluble in acids, insoluble in potash and organic solvents, which loses $5H_2O$ at 110°, and is decomposed above 300° with formation of uranosouranic oxide (compare Drenckman, *Zeit. gesammt. naturwiss.*, 17, 149). The *tetrauranate*, $K_2O, 4UO_3, 5H_2O$, is obtained directly by repeatedly evaporating a solution of potassium uranyl acetate on the water-bath until no longer acid. Sodium uranyl acetate, when heated in aqueous solution in a reflux apparatus, yields uranyl hydroxide (compare Zimmermann, *Abstr.*, 1886, 598); when evaporated on the water-bath, *sodium pentauranate*, $Na_2O, 5UO_3, 5H_2O$, is produced. Ammonium uranyl acetate has a sp. gr. 2.219 at 15° in benzene, and in aqueous solution decomposes after a short time (compare Wertheim, *loc. cit.*), or at once on heating or evaporation, forming a *hexauranate*, $(NH_4)_2U_6O_{19}, 10H_2O$, which, when heated, yields ammonia and uranosouranic oxide.

R. L. J.

Methods for the Preparation of Acrylic Acid. By EINAR BILLMANN and ALFRED WÖHLK (*J. pr. Chem.*, 1900, [ii], 61, 199).—An enumeration of the various available methods for the preparation of acrylic acid.

R. H. P.

Acrylic Acid from Glycerol. By ALFRED WÖHLK (*J. pr. Chem.*, 1900, [ii], 61, 200—214).—The various methods of preparing acrylic acid from glycerol have been reinvestigated, and are fully described.

R. H. P.

Preparation of Acrylic Acid from Allyl Alcohol. By EINAR BILLMANN (*J. pr. Chem.*, 1900, [ii], 61, 215—224).—A detailed description of the preparation of acrylic acid from allyl alcohol by means of $\alpha\beta$ -dibromopropyl alcohol and $\alpha\beta$ -dibromopropionic acid.

Manganese acrylate and *copper acrylate*, $2(C_2H_3 \cdot CO_2)_2Cu, H_2O$, are both soluble salts. The *mercuric acrylate*, $HgO, (C_2H_3 \cdot CO_2)_2Hg$, is precipitated by alcohol from a solution of mercuric oxide in dilute acrylic acid solution.

R. H. P.

γ -Chlorocrotonic Acid. By ROBERT LESPIEAU (*Compt. rend.*, 1900, 130, 1410—1411).— *γ -Chlorocrotononitrile*, $CH_2Cl \cdot CH : CH \cdot CN$, obtained by the action of phosphoric oxide on the nitrile formed by the action of hydrocyanic acid on epichlorhydrin is a colourless liquid of sp. gr. 1.1495 at 0°, which boils at 73—73.5° under 15 mm. pressure, and strongly attacks the skin. *Ethyl γ -chlorocrotonate*, obtained similarly from the ethyl salt formed when the same nitrile is hydrolysed in presence of alcohol, boils at 191—193° under 750 mm. pressure. *γ -Chlorocrotonic acid*, $CH_2Cl \cdot CH : CH \cdot CO_2H$, is a white solid with a strong odour; it melts at 76.5—77.5°, and distils in a vacuum without decomposing. It is prepared by the action of dilute alcoholic potash on the ethyl salt, and cannot be obtained by hydrolysis of the nitrile. When the latter is treated with potassium hydroxide, it loses chlorine, and when treated with hydrochloric acid it yields the dichlorobutyric acid, $CH_2Cl \cdot CHCl \cdot CH_2 \cdot CO_2H$, which melts at 45—50°. C. H. B.

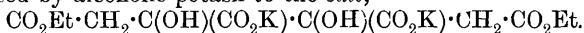
Action of Hydrogen Bromide on Ricinoleic Acid and on its Acetyl Derivative. By ALEXANDER KASANSKY (*J. Russ. Phys. Chem. Soc.*, 1900, 32, 149—155).—The action of hydrogen bromide in the cold on ricinoleic acid gives first a monobromo-acid of the composition $C_{18}H_{33}O_2Br$, and if the action be continued, a dibromostearic acid, $C_{18}H_{34}O_2Br_2$, is obtained; on reduction, both of these bromo-acids yield stearic acid. Both Krafft's (Abstr., 1888, 1270) and Goldsobel's (Abstr., 1895, i, 81) formulæ for ricinoleic acid point to the possibility of converting it, by the action of hydrogen bromide, into two isomeric dibromostearic acids; on reduction, however, those derived from Krafft's formula would give two different acids, whilst the two dibromo-acids indicated by Goldsobel's constitution for ricinoleic acid would yield one and the same product—stearic acid. The latter formula is hence supported by the author's results. On acetylating ricinoleic acid and passing hydrogen bromide into an acetic acid solution of the acetyl compound, a bromoacetyl derivative of the composition $C_{18}H_{34}O_2Br \cdot OAc$ is obtained. On reduction, this yields a *hydroxy-stearic acid*, $C_{18}H_{35}O_2 \cdot OH$, melting at $81-82^\circ$, and re-solidifying at $78.5-78^\circ$, but differing from the ordinary acid of this composition obtained from oleic or elaidic acid in its solubility in alcohol and ether; 100 parts of a 99.5 per cent. alcoholic solution saturated at 20.5° contain 13.24 parts of the acid, the number for an ethereal solution at 18.5° being 5.39. T. H. P.

Behaviour of Dibasic β -Hydroxy-acids on Boiling with Aqueous Sodium Hydroxide. By FRITZ FICHTER and CAMILLE DREYFUS (*Ber.*, 1900, 33, 1452—1455).—Dibasic β -hydroxy-acids, when boiled with 20 per cent. aqueous sodium hydroxide for 24 hours, lose water and yield unsaturated dicarboxylic acids. Thus, β -hydroxy-glutaric acid yields 50 per cent. of glutaconic acid, and malic acid 60 per cent. of pure fumaric acid. *iso*-Butylparaconic acid yields 13 per cent. of *isobutylitaconic acid*, whilst phenylparaconic acid gives a mixture of 26 per cent. of phenylitaconic acid and 40 per cent. of phenylisoparaconic acid (m. p. 168° , Fittig, this vol., i, 397); from δ -caprolactone- γ -carboxylic acid (Abstr., 1897, i, 13), a 14 per cent. yield of α -ethylideneglutaric acid (Fichter and Eggert, Abstr., 1898, i, 630) is obtained. W. A. D.

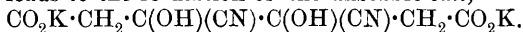
Action of Cyanogen Chloride on Ethyl Acetonedicarboxylate. By JUVÉNAL DERÔME (*Compt. rend.*, 1900, 130, 1475—1478).—The sodium derivative of ethyl cyanoacetonedicarboxylate is produced by treating ethyl acetonedicarboxylate successively with sodium ethoxide and cyanogen chloride.

Ethyl cyanoacetonedicarboxylate, obtained by the action of dilute acids on the preceding substance, is crystalline, melts at $43-44^\circ$, and is soluble in the ordinary organic solvents. This compound behaves as a monobasic acid, and yields *silver*, *copper*, and *barium* derivatives having the formulæ $C_{10}H_{12}O_5Na$, $(C_{10}H_{12}O_5N)_2Cu$, and $(C_{10}H_{12}O_5N)_2Ba$. The *ethyl* derivative, $C_{10}H_{12}O_5NEt$, obtained by the action of ethyl iodide on the silver compound, separates from an ethereal solution in colourless, silky crystals, melting at 55° ; this substance may have either a ketonic or an enolic constitution. G. T. M.

Action of Hydrocyanic Acid on Ethyl Cetipate. By RENÉ THOMAS-MAMERT and ST. WEIL (*Bull. Soc. Chim.*, 1900, [iii], 23, 430—437).—Hydrocyanic acid itself has little or no action on ethyl cetipate (oxalldiacetate), but the gradual addition of hydrochloric acid to a mixture of potassium cyanide with an ethereal solution of the ester results in the formation of about 3 per cent. of *ethyl βγ-dihydroxy-βγ-dicyanohexanedioate*, $\text{CO}_2\text{Et}\cdot\text{CH}_2\cdot\text{C}(\text{OH})(\text{CN})\cdot\text{C}(\text{OH})(\text{CN})\cdot\text{CH}_2\cdot\text{CO}_2\text{Et}$, which crystallises in large, white tablets melting at 164° , and is hydrolysed by alcoholic potash to the salt,



On the other hand, the action of potassium cyanide on oxalldiacetic acid itself, leads to the formation of the unstable salt,



The chief product, however, of the first reaction is a pale yellow, crystalline substance of the composition $\text{C}_{21}\text{H}_{25}\text{O}_{12}\text{K}$, which is probably formed by the condensation of 2 mols. of ethyl cetipate with subsequent fixation of hydrogen cyanide and hydrolysis of the compound thus formed. The corresponding acid, $\text{C}_{21}\text{H}_{26}\text{O}_{12}$, was obtained as a green, uncrystallisable oil.

The difficulty with which ethyl cetipate reacts with hydrogen cyanide suggested that the ester might have the enolic formula, $\text{CO}_2\text{Et}\cdot\text{CH}:\text{C}(\text{OH})\cdot\text{C}(\text{OH})\cdot\text{CH}\cdot\text{CO}_2\text{Et}$, but an examination of its behaviour towards benzylideneaniline (compare Schiff, *Abstr.*, 1898, i, 237), made with a view to deciding this question, gave no definite results. Experiments with benzylidene-β-naphthylamine were also indecisive, the product of the action of this compound on ethyl cetipate being a white, crystalline substance, $\text{C}_{44}\text{H}_{40}\text{N}_2\text{O}_8$, melting at 125° , whilst in the presence of a trace of piperidine a red, crystalline substance melting at 80° is obtained, which appears to have the composition $\text{C}_{88}\text{H}_{78}\text{O}_{11}\text{N}_4$, and to be a condensation product, and not an isomeride, of the compound formed in the absence of piperidine. It is also noteworthy that no definite reduction products could be obtained from ethyl cetipate, however the conditions were varied. N. L.

Compounds of Bromal with Formaldehyde. By ADOLF PINNER (*Ber.*, 1900, 33, 1432—1433).—Of several aldehydes examined, only bromal has been found to react with formaldehyde in the same way as chloral does (*Abstr.*, 1898, i, 626). About half the quantity of sulphuric acid used in the latter case was employed, and the mixture was allowed to remain for weeks; the solid product was separated by extraction with boiling alcohol into the sparingly soluble *hexabromodimethyltetroxan*, which melts far above 250° , and the soluble *hexabromodimethyltrioxin*, which melts and decomposes at 212 — 213° .

The resinous product, formerly supposed to be dichloral methylene-glycoloxide, was really an impure tetroxan. C. F. B.

Action of Bromine on Polymeric Aldehydes. I. By ADOLF FRANKE (*Monatsh.*, 1900, 21, 205—209).—Under certain conditions, paraldehydes yield derivatives without previous change to the monomeric state. Para-α-bromoisobutaldehyde (trimeric), obtained in almost theoretical quantity by adding bromine to a solution of para-isobutaldehyde in carbon disulphide cooled to -15° , crystallises from dilute

alcohol in glistening, white needles and melts at 129° (compare Lipp, *Annalen*, 1882, 211, 352), and is soluble in ether, light petroleum, benzene, acetone, or hot alcohol. It is scarcely attacked when heated with acids, alkalis, or acid dichromate solution, and metallic sodium, methylic iodide, or zinc ethyl fail to remove bromine. By continued heating at 150° , it is readily converted into the monomeric condition.

R. L. J.

2-Methyl-2-Bromopropanal [α -Bromo*isobutaldehyde*]. By ADOLF FRANKE (*Monatsh.*, 1900, 21, 210—215).—This substance, prepared by heating parabromo*isobutaldehyde* (see preceding abstract), distils in an atmosphere of carbon dioxide at 113° under 750 mm. pressure as a clear, mobile liquid of sp. gr. 1.555, which fumes in moist air and violently attacks the mucous membrane. If pure, and kept in a closed flask, it remains unaltered for weeks, but a trace of acid or moisture causes polymerisation. Acid dichromate solution removes bromine and forms α -hydroxy*isobutyric acid*; similarly, when heated with water, α -hydroxybutaldehyde is produced, which was not observed to polymerise when kept, as stated by Gorboff and Kessler (*Abstr.*, 1888, 814). α -Bromo*isobutaldehyde* reacts with hydroxylamine to form α -hydroxybutaldoxime, a thick, colourless, soluble liquid which distils at 110° under 19 mm. pressure. By the action of acetic anhydride, this oxime yields a dark, resinous oil, which is destroyed by distillation and decomposed by sodium carbonate into acetone and hydrogen cyanide.

R. L. J.

An Aldol from *iso*-Butaldehyde and Formaldehyde. By LEO WESSELY (*Monatsh.*, 1900, 21, 216—234).—By the action of potassium carbonate instead of alcoholic potash or calcium hydroxide (compare Just, *Abstr.*, 1896, i, 413; and Apel and Tollens, *Abstr.*, 1894, i, 353) on a mixture of *isobutaldehyde* and formaldehyde, an *aldol* is obtained which distils at 67 — 69° under 14 mm. pressure, and melts at 89 — 90° . It dissolves with some difficulty in many organic solvents, is oxidised by bromine water or permanganate, but not attacked by atmospheric oxygen even when left for a long time in aqueous solution. Under 747 mm. pressure, two-thirds distil over at 172 — 173° unchanged, the remaining third being decomposed into the aldehydes. The molecular weight, as determined by cryoscopic and ebullioscopic methods, indicates a dimeric aldol; by continued heating (as in a vapour density determination), it becomes monomeric, and the derivatives appear to be of the latter type. By reduction, Just's pentaglycol (*loc. cit.*) is obtained, and by oxidation with potassium permanganate, dimethylmalonic acid, together with the fourth of the five theoretically possible hydroxyvaleric acids.

The latter, which the author names *hydroxyppivalic acid*, $\text{OH}\cdot\text{CH}_2\cdot\text{CMe}_2\cdot\text{CO}_2\text{H}$, crystallises in the rhombic system, melts at 123° , dissolves sparingly in ether, and when oxidised yields dimethylmalonic acid, which melts at 185° , not at 117° , as stated in Beilstein's handbook.

The aldol forms a *triacetyl* derivative, $\text{C}_{11}\text{H}_{18}\text{O}_6$, of mol. weight 246, which distils at 136 — 137° under 12 mm. pressure, and an *oxime*, $\text{C}_5\text{H}_{11}\text{O}_2\text{N}$, which boils at 129° under 18 mm. pressure, melts at 29.5° ,

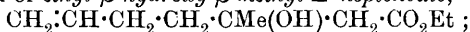
and has a molecular weight of 234 or 117, according to the temperature of estimation.
R. L. J.

The Negative Nature of Unsaturated Groups of Atoms. By FERDINAND HENRICH (*Ber.*, 1900, 33, 1435—1438).—The author (*Abstr.*, 1899, i, 469, &c.) has published the view that all unsaturated groups of atoms exert a certain negative action, rendering replaceable the hydrogen atoms of an adjacent CH_2 group. Modern opinion inclines to the view that such substitution does not take place directly in the CH_2 group of the ketonic form, but that the latter first undergoes a transformation into the tautomeric enolic form. The author points out that the two views are not incompatible, as Hantzsch and Kissel (this vol., i, 89) seem to think.
C. F. B.

Allylacetone. By JULIUS VON BRAUN and FRITZ STECHELE (*Ber.*, 1900, 33, 1472—1477).—Allylacetone prepared by Conrad's method (*Annalen*, 1878, 192, 153) and purified by means of the *semicarbazone* (m. p. 100—102°), boils at 129·5° and has a sp. gr. 0·8430; on oxidation with sodium hypobromite, it yields bromoform and allylacetic acid, whilst with 1 per cent. aqueous potassium permanganate, it gives rise to formaldehyde and lævulic acid; attempts to bring about, by means of acids and alkalis, a rearrangement of allylacetone to either methyl α -ethylideneethyl ketone, $\text{CHMe}:\text{CH}\cdot\text{CH}_2\cdot\text{CO}\cdot\text{CH}_3$, or ketohexamethylene failed; hydrogen bromide, either gaseous or dissolved in glacial acetic acid, is also without action on the ketone, methyl α -bromobutyl ketone (Lipp, *Abstr.*, 1886, 218) not being formed. Attempts to obtain the foregoing methyl α -ethylideneethyl ketone from propenyl bromide, $\text{CHMe}:\text{CHBr}$, and sodium dibromobutyrate were without issue. The *dibromide* of allylacetone is a colourless oil which decomposes when kept, and when treated with alkalis gives rise to complex decomposition products.

The *oxime* of allylacetone boils at 190°, and when reduced with sodium in ethyl alcohol yields apparently ϵ -amino- Δ^4 -hexylene ("butallylmethylcarbinamine," Merling, *Abstr.*, 1891, 1506); attempts to convert the dibromide of the latter into a pyrrolidine derivative by loss of hydrogen bromide (compare Merling, *loc. cit.*) gave no definite result. On the other hand, treatment of the foregoing oxime with phosphorus pentoxide (compare Wallach, this vol., i, 44) appears to yield dimethylpyrrolidine. When the oxime is reduced with sodium in boiling amyl alcohol, a small quantity only of β -aminohexane, boiling at 116°, is obtained, owing to complex decomposition occurring; the base was isolated in the form of the *platinichloride*.

When allylacetone is treated with ethyl bromoacetate and zinc according to Reformatsky's method (*Abstr.*, 1887, 717), it gives a 65 per cent. yield of *ethyl β -hydroxy- β -methyl- Δ^4 -heptenoate*,

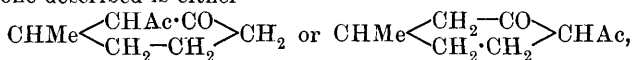


this boils at 123—125° under 20 mm. pressure, whilst the corresponding acid, $\text{C}_8\text{H}_{14}\text{O}_3$, is a colourless liquid boiling at 175° under 25 mm. pressure. On heating the latter for 6 hours with acetic anhydride containing sodium acetate, water is split off and β -methyl- α -heptadienoic acid, $\text{CH}_2:\text{CH}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{CMe}:\text{CH}\cdot\text{CO}_2\text{H}$, formed; this boils at 138—140° under 18 mm. pressure, has a sp. gr. 0·9712 at

19°, $\mu_D = 1.4604$, and yields a stable *silver* salt; with bromine in glacial acetic acid solution, it yields a *tetrabromide* as an oil, and on oxidation gives rise to formaldehyde and lævulic acid, facts which determine its structure.

W. A. D.

Cyclic β -Diketones. I. By GEORGES LESER (*Bull. Soc. Chim.*, 1900, [iii], 23, 370—374).—Three cyclic β -diketones, having one carbonyl group in the nucleus and the other in the side chain, have hitherto been described, two of these being obtained by Baeyer from menthone and tetrahydrocarvone, whilst the third, which differs from the other two in undergoing only partial hydrolysis and in not forming a copper salt, was prepared by the author (*Abstr.*, 1899, i, 743) from acetylmethylheptenone. In order to ascertain the cause of these differences in behaviour, a general method for the preparation of similar ketones was sought in the application of Claisen's reaction to cyclanones. Wallach's methylcyclohexanone, when treated with sodium and ethyl acetate, yields 25—30 per cent. of its weight of *acetylmethylcyclohexanone*, which was obtained as a colourless liquid boiling at 122° under 14 mm. pressure, and having a sp. gr. 1.030 at 12°; it has all the characteristics of β -diketones, since it is soluble in cold alkalis, gives a red coloration with ferric chloride, forms a well crystallised sodium hydrogen sulphite derivative, and yields a dioxime which melts and decomposes at 171—172°. When boiled with aqueous or alcoholic potash, it undergoes partial hydrolysis with the formation of a *ketonic acid*, $C_9H_{16}O_3$, which boils at 172—174° under 8 mm. pressure, forms a semicarbazone melting at 141—142°, and is converted by oxidation with sodium hypobromite in the cold into an acid which appears to be identical with β -methylpimelic acid. From these results, the conclusion is drawn that the acetylmethylcyclohexanone described is either



and the ketonic acid derived therefrom either



or $CH_2Ac \cdot CH_2 \cdot CH_2 \cdot CHMe \cdot CH_2 \cdot CO_2H$.

N. L.

Double Thiocyanates and Cyanides. By PAUL WALDEN (*Zeit. anorg. Chem.*, 1900, 23, 373—377).—The author has determined the electric conductivity of the following salts: potassium silver cyanide, potassium mercury cyanide, potassium zinc cyanide, potassium cadmium cyanide, sodium nitroferrocyanide, potassium nickel cyanide, potassium platinum thiocyanate, potassium cobalt cyanide, and potassium manganese cyanide. The values for $\Delta = (\mu_{1024} - \mu_{32})$ are in accordance with the view that these compounds are complex salts.

E. C. R.

Action of Cyanogen Bromide on Tertiary Amines. By JULIUS VON BRAUN (*Ber.*, 1900, 33, 1438—1452).—Cyanogen bromide reacts with tertiary amines, $NR^{11}R^{111}$. In some cases, the transient formation of a solid substance, presumably a compound, $NR^{11}R^{111}Br \cdot CN$, can be observed; in all cases, the final products are a cyanamide, $NR^{11}R^{111} \cdot CN$, and an alkyl bromide, R^1I . In the case of dimethylaniline,

and in this case only, the formation of a tetralkylammonium salt, NMe_3PhBr , was observed in amount equivalent approximately to 2 mols. per 3 of the cyanamide; without doubt, the alkyl bromide, formed as indicated above, had added itself on to some of the tertiary amine which had not yet reacted with the cyanogen bromide. In the case of tripropylamine, ethyldipropylamine, methyldipropylamine, and tribenzylamine, the hydrobromide of the amine was formed in addition to the cyanamide. It is always the smallest of the alkyl radicles that is eliminated as the alkyl bromide; this was distilled off, and then the cyanamide was distilled over under diminished pressure. The latter was identified by hydrolysing it with acid agents into the corresponding secondary amine, $\text{NHR}^{11}\text{R}^{11}$, or by converting it with alcoholic ammonia and hydrogen sulphide into the corresponding thiocarbamide, $\text{NR}^{11}\text{R}^{11}\cdot\text{CS}\cdot\text{NH}_2$.

Methyldipropylamine, ethyldipropylamine, and tripropylamine react very vigorously with cyanogen bromide; ether may be used as a diluent. Dimethylaniline, methylethylaniline, and diethylaniline react less readily, and the first somewhat abnormally, as just indicated. Methylpropylaniline, ethylpropylaniline, and dipropylaniline react still less readily. Diphenylamine does react, but the reaction has to be accelerated by heating for 2 hours at $60-70^\circ$; the same is true of tribenzylamine. Diphenylmethylamine and triphenylamine do not react at all with cyanogen bromide.

Most of the substances obtained seem to be known already. *Phenylpropylcyanamide* is, perhaps, new; it boils at $140-142^\circ$ under 10 mm., and at 281° under atmospheric pressure, decomposing slightly in the latter case.

By treating a tertiary amine with cyanogen bromide and hydrolysing the resulting cyanamide, the smallest radicle of the amine can be eliminated and a secondary amine obtained. The method is a convenient one, and may prove useful in the investigation of alkaloids.

C. F. B.

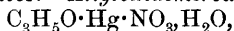
Methylisocarbamide. By JULIUS STIEGLITZ and RALPH H. MCKEE (*Ber.*, 1900, 33, 1517—1519. Compare this vol., i, 340)—A quantitative yield of methylisocarbamide hydrochloride is readily obtained by passing dry hydrogen chloride (1.08 mols.) into a solution of cyanamide (1 mol.) in methyl alcohol (25 mols.), allowing the solution to remain for 2 hours, and then distilling off the excess of alcohol at 40° . The base is a white, crystalline solid melting at $44-45^\circ$, and distilling at 82° under 9 mm. pressure; it has strong basic properties, and readily abstracts both moisture and carbon dioxide from the atmosphere. When heated with very dilute hydrochloric acid at 100° in sealed tubes, it yields methyl chloride and carbamide. The author considers that this affords an explanation of observations made by Gabriel (*Abstr.*, 1896, i, 121), and by Menne (this vol., i, 286).

Ethylisocarbamide, $\text{NH}_2\cdot\text{C}(\text{OEt})\cdot\text{NH}$, melts at 42° , and distils at $95-96^\circ$ under 15 mm. pressure.

J. J. S.

Action of Allyl Alcohol and of Ethylene on Mercuric Salts. By EINAR BILMANN (*Ber.*, 1900, 33, 1641—1655. Compare Hofmann and Sand, this vol., i, 384, 385, 386).—*Allyloxidemercuric sulphate*,

$(C_3H_5 \cdot O \cdot Hg)_2SO_4 \cdot 4H_2O$, obtained as a crystalline precipitate when allyl alcohol is mixed with a solution of mercuric oxide in sulphuric acid and the mixture kept for 2—4 hours, is readily soluble in water and in ammonium or sodium hydroxide, and may be recrystallised from boiling water. When dissolved in 20 per cent. ammonium hydroxide and mixed with three times its volume of alcohol, it yields crystals of *allyloxidemercuric ammonium sulphate*, $(C_3H_5 \cdot O \cdot Hg)_2(NH_3)_2SO_4$, which are readily soluble in water. *Allyloxidemercuric nitrate*,



obtained by the action of allyl alcohol on an excess of mercuric nitrate, forms colourless crystals, and, unlike Hofmann and Sand's compound, is readily soluble in water, also in ammonia or potassium hydroxide, the latter solutions yielding a white precipitate on the addition of ammonium sulphide. If the preparation is not made in the cold, insoluble products are obtained. *Allyloxidemercuric ammonium nitrate*, $C_3H_5 \cdot O \cdot Hg \cdot (NH_3) \cdot NO_3$, forms colourless crystals readily soluble in water, and the solution has an alkaline reaction, and when boiled evolves ammonia. *Allyloxidemercuric acetate*, $2C_3H_5 \cdot O \cdot Hg \cdot C_2H_3O_2 \cdot H_2O$, forms small, star-shaped, colourless crystals readily soluble in water; when recrystallised from hot water, it crystallises anhydrous in the form of short prisms. When solutions of the sulphate, nitrate, and acetate are treated with potassium bromide or chloride, *allyloxidemercuric bromide* and *chloride* are obtained as white precipitates. When precipitated mercuric oxide is shaken with allyl alcohol and water, an alkaline liquid is obtained which gives a precipitate with hydrobromic acid.

Ethanolmercuric sulphate, $(OH \cdot CH_2 \cdot CH_2 \cdot Hg)_2SO_4$, obtained by slowly bubbling ethylene through a solution of mercuric oxide in sulphuric acid for some hours, forms a colourless, crystalline precipitate sparingly soluble in cold water, but soluble in hot water, ammonia, or potassium hydroxide. *Ethanolmercuric bromide*, $OH \cdot CH_2 \cdot CH_2 \cdot HgBr$, is insoluble in water, but soluble in ammonia.

Various attempts to prepare Hofmann and Sand's allene compounds have been made, but without success.

The constitution of the allyl oxide compound is represented as $CH_2 \begin{array}{c} \diagup O \diagdown \\ \diagdown CH_2 \diagup \end{array} CH \cdot HgX$, as the alternative formula, $\overset{\overset{CH_2}{|}}{\underset{\underset{O}{|}}{C}} \begin{array}{c} \diagup \\ \diagdown \end{array} CH \cdot CH_2 \cdot HgX$, contains an asymmetric carbon atom, and all attempts to resolve the compound into optically active constituents by the aid of *d*-tartaric acid have been unsuccessful. J. J. S.

Iodoso-, Iodoxy-, and Iodonium Compounds derived from Iodo- and Chloriodo-mesitylene. By CONRAD WILLGERODT and HEINRICH ROGGATZ (*J. pr. Chem.*, 1900, [ii], 61, 423—430).—*Iodoso-mesitylene*, $C_6H_2Me_3 \cdot IO$, a greyish-yellow, amorphous mass of characteristic odour, is only slightly soluble in most solvents and decomposes on keeping into iodomesitylene and iodoxyesitylene. The *chloride*, $C_6H_2Me_3 \cdot ICl_2$, crystallises in yellow needles, and rapidly changes into chloriodomesitylene. The *acetate*, $C_6H_2Me_3 \cdot I(OAc)_2$, crystallises from acetic acid in white needles, melts at 158° , and is fairly stable. The yellow *chromate* explodes before it is completely dry.

Iodosomesitylene, $C_6H_2Me_3 \cdot IO_2$, prepared by warming iodosomesitylene with chloroform, or alone, or in a current of steam, crystallises from acetic acid in white needles and explodes at 195° .

Dimesityliodonium hydroxide, $I(C_6H_2Me_3)_2 \cdot OH$, was prepared by grinding a molecular mixture of iodosomesitylene and iodoxyesitylene with moist silver oxide. The *chloride* crystallises from alcohol in needles, melts at 122° , and is insoluble in water. The *bromide* crystallises from alcohol in yellow needles and melts at 139° . The *iodide* is an amorphous, yellow precipitate insoluble in water or ether, and melts at 194° . The *nitrate* melts at 126° . The *hydrogen sulphate*, $I(C_6H_2Me_3)_2 \cdot HSO_4$, crystallises in long, white flakes, and melts at 167° . The *chromate* is a yellow, amorphous precipitate, and decomposes at 101° . The *platinichloride*, $[I(C_6H_2Me_3)_2]_2PtCl_6$, is a yellow, amorphous powder which decomposes at 151° . The *mercurichloride*, $[I(C_6H_2Me_3)_2Cl]_2HgCl_2$, decomposes at 130° .

Phenylmesityliodonium hydroxide, $C_6H_2Me_3 \cdot IPh \cdot OH$, was prepared from iodoxybenzene and iodosomesitylene. The *chloride* crystallises from alcohol and melts at 94° . The *mercurichloride* crystallises from hot water in white needles and decomposes at 247° . The *platinichloride* melts at 173° .

Dichloroethylmesityliodonium chloride, $C_6H_2Me_3 \cdot ICl \cdot C_2H_3Cl_2$, prepared by the action of mesityliodosochloride on a compound of silver acetylide and silver chloride suspended in water, crystallises in white flakes and melts at 149° . The *platinichloride* forms yellow needles and melts at 133° .

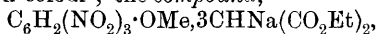
Chloroiodosesitylene, prepared by the action of chlorine on iodosesitylene at the ordinary temperature, crystallises from chloroform in white needles, and melts at 180° . *Chloroiodosomesitylene*, $C_6HMe_3Cl \cdot IO$, resembles iodosomesitylene; the *chloride*, $C_6HMe_3Cl \cdot ICl_2$, crystallises from benzene in yellow needles, and readily decomposes into chloroiodosesitylene, the chlorine being liberated instead of passing into the nucleus; the *acetate* crystallises from acetic acid in white needles and melts at 169° . *Chloroiodoxyesitylene*, $C_6HMe_3Cl \cdot IO_2$, separates from acetic acid in an amorphous state and melts without exploding at 222° .

T. M. L.

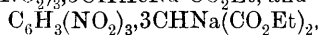
Certain Coloured Substances derived from Nitro-compounds. By C. LORING JACKSON and F. H. GAZZOLO (*Amer. Chem. J.*, 1900, 23, 376—396. Compare Abstr., 1899, i, 744).—The coloured substances resulting from the action of sodium alkyl oxides on certain nitro-compounds were considered by Meyer (*Ber.*, 1894, 27, 3156) to be formed by the replacement of a hydrogen atom of the benzene nucleus by the sodium atom, but this view was shown to be incorrect by Lobry de Bruyn (Abstr., 1895, i, 653). Hantzsch and Kissel (this vol., i, 89) regard them as additive compounds in which the sodium alkyl-oxide is added to the nitro-group, whereas the observations of the present authors are best explained on the hypothesis that the carbon of the benzene nucleus, as well as the nitro-group, is involved, and that the substances possess a quinonoid structure.

When a solution of trinitroanisole or trinitrobenzene in benzene is

treated with a solution of ethyl sodioacetoacetate or sodiomalonate in the same solvent, a red precipitate is produced which consists of a compound of 1 mol. of the nitro-compound with 3 mols. of the ethereal salt. These substances are amorphous powders, soluble in water, alcohol, or acetone; they explode on heating, and are instantly decomposed by acids. The compound, $C_6H_2(NO_2)_3 \cdot OMe, 3CHAcNa \cdot CO_2Et$, is of a deep crimson colour; the compound,



possess a deep maroon colour, and does not react with ethyl iodide. The compounds, $C_6H_3(NO_2)_3, 3CHAcNa \cdot CO_2Et$, and



are of a brownish-red and a rich maroon colour respectively; the latter is decomposed by bromine with formation of trinitrobenzene and sodium bromide.

The compound, $C_6H_3(NO_2)_3, 3C_5H_{11} \cdot ONa$, obtained by the action of sodium amyloxyde on trinitrobenzene, is a dark crimson, amorphous powder, soluble in water, alcohol, or acetone. Sodium methoxide and ethoxide yield similar products, whilst sodium phenoxide produces a red colour, but no precipitate. Coloured substances are also formed by the action of sodium hydroxide and benzyl cyanide on trinitrobenzene, but cannot be isolated. When picramide is treated with sodium methoxide, a brick-red precipitate is obtained, which rapidly decomposes. 2:4-Dinitrotoluene gives a very unstable, red precipitate both with sodium methoxide and with ethyl sodiomalonate. 2:4-Dinitro-*m*-xylene produces a coloration with sodium methoxide, but not with ethyl sodioacetoacetate or sodiomalonate; 2:4:6-trinitro-*m*-xylene yields an unstable red substance with each of these reagents, whilst dinitromesitylene, trinitromesitylene, and the triethyl ether of dinitrophloroglucinol give only negative results.

Similar experiments were made with aromatic compounds rich in negative radicles, but not containing nitro-groups, but in no case was any coloured additive compound produced.

When the compound $C_6H_2(NO_2)_3 \cdot OC_7H_7, C_7H_7 \cdot ONa$ (Abstr., 1898, i, 517) is heated with methyl alcohol, both the benzyl groups are replaced by methyl, and on treating the methyl compound with benzyl alcohol the reverse change occurs. Benzyl picrate melts at 145° , and not at 115° , as inadvertently stated (*loc. cit.*). Benzoyl chloride reacts with the methyl compound, $C_6H_2(NO_2)_3 \cdot OMe, OMeNa$, with the formation of a substance of a more intense scarlet colour.

The paper also contains the description of an improved method for the preparation of picryl chloride. E. G.

Alkylation of Indene. By WILHELM MARCKWALD (*Ber.*, 1900, 33, 1504—1505)—The indenenes can be alkylated by the action of alkyl iodides in presence of solid alkali hydroxides.

1-Benzylindene, $CH \leq \begin{smallmatrix} C_6H_4 \\ CH \end{smallmatrix} > CH \cdot CH_2Ph$, prepared by the action of benzyl chloride and solid potassium hydroxide on indene, is a yellow oil which boils at $230-235^\circ$ under 15 mm. pressure.

1-Methylindene boils at $197-200^\circ$, and, unlike indene, is lighter

than water; it gives a series of colour reactions with sulphuric acid, which serve to distinguish it from indene and the isomeric 3-methylindene.

T. M. L.

Oxidation of Aniline. By EUGEN BAMBERGER and FRED. TSCHIRNER (*Annalen*, 1900, 311, 78—90. Compare Abstr., 1898, i, 518, and Abstr., 1899, i, 347).—The paper describes in detail the experimental results, of which a summary has already appeared (*loc. cit.*).

M. O. F.

Direct Introduction of Nitro-groups into the Side Chain of Aromatic Amines. By EUGEN BAMBERGER and ERNST HOFF (*Annalen*, 1900, 311, 91—98. Compare Abstr., 1894, i, 239; also Abstr., 1895, i, 261, 273).—The paper contains experimental details relating to the action of nitric anhydride on *o*-toluidine, *p*-toluidine, ψ -cumidine, and *p*-nitraniline (compare *loc. cit.*). M. O. F.

Dehydration of Amine Nitrates to Nitramines (Diazoic Acids). By EUGEN BAMBERGER and ERNST HOFF (*Annalen*, 1900, 311, 99—116).—When the nitrates of certain amines are heated with acetic anhydride, the elements of water are eliminated, and nitramines (diazoic acids) produced (Bamberger, Abstr., 1895, i, 273). The yield of a diazoic acid, depending on its tendency to undergo isomeric change, reaches a maximum in the case of *o*-nitraniline and *p*-nitraniline; α -naphthylamine and β -naphthylamine do not undergo the change in question.

The course of the reaction has been studied in the case of aniline, *o*-toluidine, *p*-toluidine, *p*-bromoaniline, *o*-nitroaniline, *m*-nitroaniline, *p*-nitroaniline, *m*-nitro-*o*-toluidine, *m*-nitro-*p*-toluidine, *p*-chloroaniline, and *p*-chloro-*o*-nitroaniline.

M. O. F.

Action of Cyanogen Bromide on Dimethyl- and Diethyl-aniline. By ROLAND SCHOLL and WILHELM NÖRR (*Ber.*, 1900, 33, 1550—1554).—Cyanogen bromide reacts with dimethylaniline at the ordinary temperature to form methyl bromide, which combines with the excess of the dimethylaniline, and *methylcyanoaniline*, $\text{NMePh}\cdot\text{CN}$, which crystallises in colourless plates melting at 31—32°; this is also formed by the action of cyanogen bromide on methylaniline. Ethylaniline behaves in a similar manner towards cyanogen bromide, ethylcyanoaniline being produced, together with ethyl bromide, only a small portion of which, however, unites with the excess of the base.

A. H.

Molecular Rearrangement of Imino-ethers by Heat. By WILHELM WISLICENUS and MAX GOLDSCHMIDT (*Ber.*, 1900, 33, 1467—1471. Compare Wheeler, this vol., i, 293).—Phenylformiminoethyl ether, $\text{OEt}\cdot\text{CH}\cdot\text{NPh}$, when heated in a sealed tube for 8 hours at 230—240°, yields 40 per cent. of the isomeric methylformanilide, a small quantity of diphenylformamidine being also formed; the transformation of phenylformiminoethyl ether into ethylformanilide is somewhat more complete (65 per cent.) under similar conditions, whilst phenylbenziminomethyl ether, $\text{OMe}\cdot\text{CPh}\cdot\text{NPh}$, yields 35 per cent. of the theoretical quantity of methylbenzanilide. From these

transformations, it appears that in the alkyl derivatives of the acid amides the stable position of the alkyl radicle is in attachment to nitrogen; the silver derivatives, on the other hand, must be regarded as O-derivatives, since in the cold they give O-ethers, although the application of heat suffices to convert the latter into N-ethers. Since benziminomethyl ether is decomposed, by heating at 270—280°, into benzonitrile and methyl alcohol, it appears that the foregoing transformations by heat are fundamentally different to the conversion of imino-ethers into acid amides by warming with alkyl iodides; in the latter case, the change takes place owing to the formation of an intermediate additive compound (Wheeler, *loc. cit.*). W. A. D.

Action of Cyanogen Bromide on Phenol. By ROLAND SCHOLL and WILHELM NÖRR (*Ber.*, 1900, 33, 1555).—When phenol is heated at 130° with cyanogen bromide, it yields *p*-bromophenol. Resorcinol behaves in a similar manner, yielding monobromoresorcinol.

A. H.

Nitroso-orcinol. By FERDINAND HENRICH (*Ber.*, 1900, 33, 1433—1435. Compare Abstr., 1896, i, 476; 1897, i, 404; and this vol., i, 163).—The red (β) variety, as prepared by the author's method, is probably as pure as that prepared by Farmer and Hantzsch (this vol., i, 103), for it changes comparatively suddenly into the yellow (α) variety at 126—129° if only a whole crystal of it be heated. When the powdered substance is heated, the change occurs at 90—110°, a partial change having taken place during the powdering. The author's value of the dissociation constant of the yellow variety differs more from that of Farmer and Hantzsch than might be expected, and it is not impossible that the latter were working with the red variety.

C. F. B.

Reactions of Formaldehyde. By CARL GOLDSCHMIDT (*Chem. Zeit.*, 1900, 24, 145. Compare this vol., i, 285).—*Anhydro-p-acetylaminobenzyl alcohol* is formed when acetanilide is boiled with excess of formaldehyde (40 per cent.) and a little dilute sulphuric acid for some time, and the red liquid thus obtained treated with alkali; it is best purified by solution in chloroform and precipitation with ether.

When resorcinol is treated with an excess of formaldehyde in the presence of dilute mineral acids, a reddish-brown compound, $C_{17}H_{16}O_6$, is obtained; it is insoluble in all the ordinary solvents; acids turn it brick-red, and alkalis purple-red (compare Caro, Abstr., 1892, 855).

J. J. S.

Action of Formaldehyde on Methylaniline. By CARL GOLDSCHMIDT (*Chem. Zeit.*, 1900, 24, 284. Compare this vol., i, 285, and preceding abstract).—When monomethylaniline is treated with an excess of formaldehyde in the presence of hydrochloric acid, colourless crystals are obtained; these dissolve in water, and are reprecipitated on the addition of hydrochloric acid. Alkalis convert the crystals into amorphous *p-anhydromethylaminobenzyl alcohol*, $CH_2:C_6H_4:NMe$,

which dissolves in chloroform, but is insoluble in ether, and melts and decomposes at 196° .
J. J. S.

Benzoyl Hydrogen Peroxide. Oxidation of Benzaldehyde in Air. By ADOLF VON BAEYER and VICTOR VILLIGER (*Ber.*, 1900, 33, 1569—1585).—Benzoyl peroxide was prepared by the action of benzoyl chloride and sodium hydroxide on hydrogen peroxide (von Pechmann and Vanino, *Abstr.*, 1894, i, 416), and when purified by dissolving in chloroform and precipitating with methyl alcohol was found to be without odour, and only very slightly soluble in water. On adding alcoholic sodium ethoxide to an ethereal solution of the peroxide, it was converted into ethyl benzoate and *benzoyl sodium peroxide*, $C_6H_5 \cdot CO \cdot O \cdot ONa$, which separated as a fine powder. This was dissolved in water, acidified, and extracted with chloroform, when a crude *benzoyl hydrogen peroxide*, $C_6H_5 \cdot CO \cdot O \cdot OH$, was obtained; when pure, this forms crystals melting without decomposition at 41 — 43° , liquefies in contact with water to a heavy oil, but is moderately stable when dry, and does not liquefy in air, dissolves easily in all solvents except light petroleum, from which it separates in leaflets, sublimes readily at the ordinary temperature, distils at 97 — 110° under 13 — 15 mm. pressure, leaving behind a certain amount of benzoic acid as a product of decomposition, and decomposes completely into benzoic acid when heated to 80 — 100° in the air. Unlike benzoyl peroxide, it has a strong, unpleasant odour resembling that of hypochlorous acid rather than that of ozone, and the vapour turns starch-iodide paper blue. It does not explode when struck, and decomposes without violence when heated; it is not decomposed by manganese dioxide, silver, or platinum, and does not oxidise chromic acid; it liberates iodine from an acid solution of potassium iodide, and more slowly from a solution to which a bicarbonate has been added, oxidises sulphurous acid, hydrochloric acid, ferrous acetate, and manganous acetate, turns litmus red and gradually bleaches it, decolorises indigo-tincture very rapidly, oxidises aniline to nitrosobenzene, benzaldehyde to benzoic acid, and menthone to mentholactone, but does not act on acetone or camphor. With benzoyl chloride and sodium hydrogen carbonate, it gives benzoyl peroxide, whilst with acetic anhydride it gives acetyl benzoyl peroxide. An *acid sodium salt* is produced by the action of carbonic, acetic, or sulphuric acid on the neutral sodium salt; it separates as a thick paste of flaky crystals, and soon decomposes into oxygen, sodium benzoate, and benzoic peroxide.

It is suggested that in the spontaneous oxidation of benzaldehyde in air, the first product is benzoyl hydrogen peroxide, and that this usually oxidises another molecule of benzaldehyde to benzoic acid, so that $1C_6H_5 \cdot CHO$ is oxidised by 1 atom of oxygen; if indigo is present, however, the benzoyl hydrogen peroxide oxidises this in preference to benzaldehyde, and $1C_6H_5 \cdot CHO$ requires O_2 for oxidation; similarly, in presence of acetic anhydride, acetyl benzoyl peroxide is produced (Nef, *Abstr.*, 1898, i, 109), and $1C_6H_5 \cdot CHO$ again requires O_2 for oxidation; the occurrence of these changes has been verified by experiment.

T. M. L.

Action of Aldehydes on Phenylacetic Acid and Benzyl Cyanide and some of its Derivatives with the Formation of Stilbene and Stilbene Derivatives. By REINHOLD VON WALTHER and A. WETZLICH (*J. pr. Chem.*, 1900, [ii], 61, 169—198. Compare Abstr., 1898, i, 321).—Details are now given for the preparation of stilbene from benzaldehyde and phenylacetic acid. When treated with silver nitrate in acetic acid solution, stilbene dibromide yields *hydrobenzoin dinitrate*, which is a colourless, microcrystalline powder melting at 132°. Anisaldehyde and phenylacetic acid, when heated together for 8 hours in a sealed tube at 240°, give a 20 per cent. yield of *p*-methoxystilbene. In a similar manner, cuminaldehyde and salicylaldehyde condense with phenylacetic acid to form *p*-isopropylstilbene and 4-phenylcoumarin respectively.

p-Nitrophenylacetic acid condenses (a) with benzaldehyde to form *α*-*p*-nitrophenylcinnamic acid, which crystallises in needles melting at 224·5°, forms insoluble silver, copper, lead, ferrous and ferric salts, an ethyl ester melting at 86°, and a methyl ester melting at 104°, but does not yield nitrostilbene when heated; (b) with anisaldehyde to form *p*-methoxy-*p*-nitrostilbene, which crystallises in lustrous, golden leaflets melting at 133°; (c) with cuminaldehyde to form *p*-isopropyl-*p*-nitrostilbene, which crystallises in small, lustrous, deep yellow leaflets melting at 132°; and (d) with salicylaldehyde to form *p*-nitro-4-phenylcoumarin, which forms yellow crystals melting at 262°.

p-Chlorobenzyl cyanide condenses (a) with benzaldehyde to form *α*-*p*-chloro-phenylcinnamionitrile, which forms colourless prisms melting at 112·5°; (b) with anisaldehyde to form *α*-*p*-chlorophenyl-*p*-methoxycinnamionitrile, which crystallises in broad prisms melting at 127·5°, and yields a dibromide which forms colourless, silky prisms which melt at 164·5°; (c) with furfuraldehyde to form *β*-furfuryl-*α*-*p*-chlorophenylacrylonitrile, which crystallises in long, yellowish, matted needles melting at 80°; (d) with piperonaldehyde to form *α*-*p*-chlorophenylmethylenedioxycinnamionitrile, which melts at 165°; (e) with *o*-nitrobenzaldehyde to form *α*-*p*-chlorophenyl-*o*-nitrocinnamionitrile, which forms bright green aggregates of silky, hair-like crystals melting at 161°; (f) with *m*-nitrobenzaldehyde to form *α*-*p*-chlorophenyl-*m*-nitrocinnamionitrile, which crystallises in yellow, prismatic plates melting at 191°; (g) with *p*-nitrobenzaldehyde to form *α*-*p*-chlorophenyl-*p*-nitrocinnamionitrile, which forms yellow needles melting at 166°; (h) with cuminaldehyde to form *α*-*p*-chlorophenyl-*p*-isopropylcinnamionitrile, which crystallises in plates or tablets frequently twinned, which melt at 126°; and (i) with bromoanisaldehyde to form *α*-*p*-chlorophenyl-*p*-methoxybromocinnamionitrile, which melts at 164°. The condensation products of piperonaldehyde with benzyl cyanide and *p*-nitrobenzyl cyanide melt at 122° and at 187° respectively.

iso-Nitroso-*p*-chlorobenzyl cyanide, $C_6H_4Cl \cdot C(CN) : NOH$, obtained by the action of amyl nitrite on *p*-chlorobenzyl cyanide, crystallises in concentric groups of needles, melts at 110°, and forms an unstable silver, but more stable sodium and copper derivatives.

Ethyl *p*-chlorophenylacetate crystallises in needles, melts at 32°.

and boils at 260°. The corresponding *methyl* ester is liquid and boils above 200°. *p*-Chlorophenylacetic acid condenses with aromatic aldehydes to form stilbene derivatives, but the intermediate acid compounds cannot be obtained; it condenses (a) with benzaldehyde to form *p-chlorostilbene*, which crystallises from glacial acetic acid and melts at 129°; (b) with anisaldehyde to form *p-methoxy-p-chlorostilbene*, which crystallises in leaflets melting at 177·5°, and forms a *dibromide* which crystallises in small, white needles; (c) with salicylaldehyde to form *3-p-chlorophenylcoumarin*, which crystallises in clusters of reddish prisms melting at 184°; and (d) with bromoanisaldehyde (which melts at 52°) to form *p-methoxybromostilbene*, which crystallises in lustrous leaflets melting at 138°. R. H. P.

New Drugs. [Aromatic Hydroxy-acids and Esters.] By ALFRED EINHORN (*Annalen*, 1900, 311, 26—77).—This paper is the first of a series having a similar character, and describes experiments undertaken with the object of introducing new drugs, and of examining certain of those already known with the view of nullifying disagreeable after-effects.

[With BALTHASAR PFYL].—*Methyl o-hydroxy-m-aminobenzoate* crystallises from a mixture of benzene and petroleum in white needles, and melts at 90°; the *ethyl* ester crystallises from alcohol, and melts at 47°.

p-Amino-m-hydroxybenzoic acid, prepared by reducing Griess' *p*-nitro-*m*-hydroxybenzoic acid with tin and hydrochloric acid, crystallises from dilute alcohol in brown leaflets, and melts at 216°; the *methyl* ester, known commercially as '*orthoform*,' crystallises from benzene or water in silvery leaflets, and melts at 120—121°; this is also obtained by reducing *methyl p-nitro-m-hydroxybenzoate*, which crystallises from alcohol in needles, and melts at 92°. The *ethyl* ester crystallises in silvery leaflets, and melts at 98°.

Methyl m-amino-p-hydroxybenzoate, known commercially as '*orthoform neu*,' is dimorphous, the technical product being in the form of lustrous needles which melt at 142°; it also separates from chloroform in white crystals which melt at 110—111°, and after solidification at 142°. The *hydrochloride* of this salt crystallises from alcohol in white needles and melts at 225°. The *ethyl* ester is likewise dimorphous, crystallising from chloroform with a small proportion of petroleum in aggregates of lustrous needles melting at 84°, whilst glacial acetic acid deposits it in leaflets melting at 112° (compare Auwers and Röhrig, *Abstr.*, 1897, i, 341).

Ethyl nitro-o-cresotate [$\text{NO}_2:\text{Me}:\text{OH}:\text{CO}_2\text{H}=5$ or $6:3:2:1$], prepared by the action of nitric acid in glacial acetic acid on *ethyl cresotate* in the same solvent, crystallises from dilute alcohol in slender plates and melts at 63—64°. *Ethyl amino-o-cresotate*, obtained on reducing the foregoing ester with tin and hydrochloric acid, crystallises from dilute alcohol in slender needles and melts at 102°.

Ethyl nitro-m-cresotate crystallises from dilute alcohol in slender, white needles, and melts at 73—74°; *ethyl amino-m-cresotate*, obtained from it on reduction, crystallises from alcohol in long, white needles melting at 85°, and therefore differs from the *ethyl aminocresotate* described by Gattermann (*Abstr.*, 1894, i, 504), which melts at 71—72°.

Nitro-p-cresotic acid crystallises from benzene or dilute alcohol in slender, reddish-yellow needles, and melts at 175° ; the *ethyl* ester forms lustrous, pale yellow leaflets, and melts at $104\text{--}105^{\circ}$. *Ethyl amino-p-cresotate* separates from alcohol in white needles and melts at 101° .

3-Hydroxy-o-toluic acid [$\text{CO}_2\text{H}:\text{Me}:\text{OH}=1:2:3$] melts at $145\text{--}146^{\circ}$; when dissolved in glacial acetic acid and treated with a mixture of glacial acetic and concentrated nitric acids, it yields two nitro-derivatives.

α -Nitro-3-hydroxy-o-toluic acid crystallises from dilute alcohol in slender, yellow needles, and melts at 182° . Reduction with tin and hydrochloric acid converts it into *α -amino-3-hydroxy-o-toluic acid*, which crystallises from water in aggregates of needles, and melts at $202\text{--}204^{\circ}$, when it decomposes; the *methyl* and *ethyl* esters melt at 129° and $109\text{--}110^{\circ}$ respectively.

β -Nitro-3-hydroxy-o-toluic acid crystallises from water in aggregates of prisms, and softens at 100° , afterwards becoming solid, and finally melting at 208° , when it darkens and evolves gas. Reduction converts it into *β -amino-3-hydroxy-o-toluic acid*, which crystallises from water in prisms, and melts at $221\text{--}222^{\circ}$; its probable constitution [$\text{CO}_2\text{H}:\text{Me}:\text{OH}:\text{NH}_2=1:2:3:6$] is indicated by the fact that it does not yield esters when the alcoholic solutions are treated with mineral acids.

Ethyl 3-hydroxy-o-toluate forms prismatic crystals, and melts at 69° . Nitration yields two derivatives, of which *ethyl β -nitro-3-hydroxy-o-toluate* is less readily soluble in water, and melts at $143\text{--}145^{\circ}$; reduction converts this substance into *ethyl β -amino-3-hydroxy-o-toluate*, which crystallises from benzene in aggregates of pale yellow, feathery crystals and melts at 113° . *Ethyl α -nitrohydroxytoluate* forms yellow needles and melts at 72° .

5-Hydroxy-o-toluic acid [$\text{CO}_2\text{H}:\text{Me}:\text{OH}=1:2:5$] melts at $183\text{--}184^{\circ}$, Kalle and Jacobsen giving 179° and 172° respectively. Nitration converts it into *α -nitro-5-hydroxy-o-toluic acid*, which crystallises from alcohol in yellow, lustrous needles melting at $163\text{--}164^{\circ}$, and *β -nitro 5-hydroxy-o-toluic acid*, separating from ethyl acetate in yellow prisms which melt at $196\text{--}197^{\circ}$; the *ethyl* esters are obtained from ethyl 5-hydroxy-o-toluate by direct nitration, the β -compound being an oil, whilst the α -ester crystallises from alcohol in yellow needles and melts at $77\text{--}79^{\circ}$. Tin and alcoholic hydrochloric acid reduce the esters to the corresponding *amino*-compounds, of which the α -derivative melts at $92\text{--}94^{\circ}$; the β -compound melts at 52° and forms a crystalline hydrochloride which melts and decomposes at $110\text{--}111^{\circ}$.

Ethyl nitroprotocatechuate crystallises from chloroform in aggregates of needles and melts at 165° . Reduction converts it into *ethyl aminoprotocatechuate*, which separates from a mixture of benzene and petroleum in pale pink needles and melts at $89\text{--}90^{\circ}$; the *hydrochloride* forms white leaflets melting at 220° .

Methyl nitroguaiacolcarboxylate, prepared by adding a mixture of glacial acetic and concentrated nitric acids to a solution of methyl guaiacolcarboxylate in glacial acetic acid, crystallises from dilute alcohol in yellow needles melting at 135° . *Methyl aminoguaiacolcarb-*

oxylate separates from benzene in long, yellow needles and melts at 130°.

Ethyl nitrodimethyl-a-resorcyrate $[\text{COEt}:\text{NO}_2:(\text{OMe})_2 = 1:4:3:5]$ forms pale yellow needles melting at 130°. *Ethyl aminodimethyl-a-resorcyrate*, prepared by reducing the foregoing ester, crystallises from ether in aggregates of needles melting at 49–50°; the hydrochloride separates from acetone in white needles.

Methyl nitro-a-naphtholcarboxylate crystallises from glacial acetic acid in small, yellowish needles and melts at 161°; reduction converts it into *methyl amino-a-naphtholcarboxylate*, melting at 128–129°.

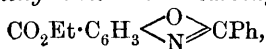
Methyl 8-hydroxyquinolinecarboxylate crystallises from benzene in white prisms and melts at 140°; the *ethyl* ester melts at 87°. When a mixture of nitric and glacial acetic acids is added to a solution of the methyl salt in acetic acid, the *acetate* of methyl nitro-8-hydroxyquinolinecarboxylate crystallises in yellow needles; at 100°, this compound loses acetic acid, yielding *methyl nitro-8-hydroxyquinolinecarboxylate*, which crystallises from alcohol in aggregates of small needles and melts at 191°. Reduction gives rise to *methyl amino-8-hydroxyquinolinecarboxylate*, which is deposited by benzene in groups of minute needles melting at 120–121°.

Methyl 5-nitro-2-benzoyloxybenzoate, prepared by the action of benzoyl chloride on methyl 5-nitrosalicylate, crystallises from alcohol or petroleum in large, well-formed prisms melting at 117–118°; unlike the substance from which it is prepared, and which also melts at 117°, the benzoyl derivative is insoluble in sodium hydroxide. *Methyl 5-amino-2-benzoyloxybenzoate* separates from alcohol in six-sided plates or prisms and melts at 176°.

Ethyl 3-nitro-4-acetoxybenzoate crystallises from dilute alcohol or acetic acid in silvery leaflets and melts at 39°. Reduction converts it into *ethyl 1-methylbenzoxazole-4-carboxylate*, $\text{CO}_2\text{Et}\cdot\text{C}_6\text{H}_3\langle\text{N}\rangle\text{CMe}$, which separates from ether in slender, white needles and melts at 50°; treatment with boiling acetic acid or dilute alcohol adds the elements of water to this compound, producing *ethyl 3-acetylamino-4-hydroxybenzoate*, crystallising in aggregates of minute rhombs or prisms and melting at 199°. The latter substance may be reconverted into the anhydro-ester by heating it with zinc chloride in an oil-bath.

Ethyl 3-nitro-4-isobutyroxybenzoate is a colourless oil yielding, on reduction, *ethyl 3-isobutyrylamino-4-hydroxybenzoate*, which crystallises from alcohol or benzene in white needles melting at 135–136°; the neutral product of reduction is *ethyl 1-isopropylbenzoxazole-4-carboxylate*, $\text{CO}_2\text{Et}\cdot\text{C}_6\text{H}_3\langle\text{N}\rangle\text{C}\cdot\text{Pr}^\beta$, which boils at 20° in a vacuum.

Methyl 3-nitro-4-benzoyloxybenzoate crystallises from alcohol in white needles and melts at 95°. Reduction converts it into *methyl 3-benzoylamino-4-hydroxybenzoate*, which separates from methyl alcohol in aggregates of leaflets and melts at 241°; the neutral product of reduction is *methyl 1-phenylbenzoxazole-4-carboxylate*,



which crystallises from alcohol in white needles and melts at 157—158°.

[With Hugo Hütz.]—4-i-Amylamino-3-hydroxybenzoic acid, prepared by gradually adding 'orthoform' dissolved in amyl alcohol to a small proportion of boiling alcohol, into which sodium is being thrown in small quantities, crystallises from benzene in white needles melting at 171—172°, and forms the *nitroso*-derivative melting at 152—153°; the *ethyl* ester crystallises in white needles and melts at 108—109°.

3-i-Amylamino-4-hydroxybenzoic acid, prepared in the same way from methyl *m*-amino-*p*-hydroxybenzoate, the structural isomeride of 'orthoform,' is a brown, amorphous compound yielding a crystalline *hydrochloride* which decomposes at 238°. The *nitroso*-derivative forms lustrous, pink leaflets and decomposes at 157—158°; the *ethyl* ester crystallises from benzene, on adding petroleum, in brownish needles melting at 69—71°.

M. O. F.

Formation of Chains. L. The Three Sodium Nitrophenoxides. By CARL A. BISCHOFF [and, in part, FRÄNKEL, GOHS, and WENGEL] (*Ber.*, 1900, 33, 1591—1602).—*Ethyl α-o-nitrophenoxypropionate*, $\text{NO}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{O} \cdot \text{CHMe} \cdot \text{CO}_2\text{Et}$, crystallises from alcohol in needles and melts at 48°; the *acid* crystallises from dilute alcohol in pale yellow needles and melts at 157—159°; *methylphenomorpholone*,

$\text{C}_6\text{H}_4 \begin{smallmatrix} \text{NH} \cdot \text{CO} \\ \diagup \quad \diagdown \\ \text{O} \quad \text{CHMe} \end{smallmatrix}$, prepared by reducing the ester with zinc dust and hydrochloric acid, crystallises from dilute alcohol in minute needles, melts at 143—144°, and dissolves readily in most organic solvents, or in strong acids. The *m-ester* is a heavy, brownish oil, which boils with partial decomposition at 187° under 7 mm., and at 295—296° under 769 mm. pressure; the *m-acid* forms yellow needles, melts at 107—110°, and decomposes gradually in the air. The *p-ester* crystallises from alcohol in small, colourless needles, melts at 59—61·5°, and boils at 195·5° under 4 mm. pressure; the *p-acid* crystallises from ether and benzene in colourless, felted needles and melts at 142·5—143°.

Ethyl α-o-nitrophenoxybutyrate, $\text{NO}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{O} \cdot \text{CHEt} \cdot \text{CO}_2\text{Et}$, melts at 40° and resembles the propionate; the *acid* crystallises from dilute alcohol in pale yellowish flakes and melts at 99—101°; on reducing with zinc dust and hydrochloric acid, chlorination takes place, and

ethyl chlorophenomorpholone, $\text{C}_6\text{H}_3\text{Cl} \begin{smallmatrix} \text{NH} \cdot \text{CO} \\ \diagup \quad \diagdown \\ \text{O} \quad \text{CHEt} \end{smallmatrix}$, is produced; this crystallises from alcohol in colourless needles and melts at 144—146°. The *m-ester* is a yellow oil which boils with partial decomposition at 184·5° under 5 mm. pressure; the *m-acid* crystallises from a mixture of ether and light petroleum in aggregates of yellow needles, melts at 94·5—95·5°, and decomposes on exposure to the air. The *p-ester* is a clear, yellow oil, and boils at 207—208° under 18 mm. pressure; the *acid* crystallises from hot water in flakes or needles and melts at 116°.

o-Nitrophenyl isobutyrate, $\text{CHMe}_2 \cdot \text{CO} \cdot \text{O} \cdot \text{C}_6\text{H}_4 \cdot \text{NO}_2$, prepared by the action of isobutyryl chloride on sodium *o*-nitrophenoxide, is a yellow oil and boils at 163—164° under 9 mm. pressure.

Ethyl α-m-nitrophenoxyisobutyrate, $\text{NO}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{O} \cdot \text{CMe}_2 \cdot \text{CO}_2\text{Et}$, is a

yellow oil and boils at 175.8° under 5 mm. pressure; the *acid* crystallises from a mixture of ether and light petroleum in yellow prisms and melts at 97.7 — 98° . The *p-ester* is an oil which boils at 190° under 13 mm. pressure; the *acid* crystallises from hot water in prisms.

Ethyl α -o-nitrophenoxyisovalerate, $\text{NO}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{O} \cdot \text{CHPr}^s \cdot \text{CO}_2\text{Et}$, is an oil which boils at 198 — 208° under 8 mm. pressure; the *acid* crystallises in needles and melts at 83 — 85° . The *m-ester* is a yellowish-brown oil, and boils at 187° under 6.5 mm. pressure; the *acid* crystallises from light petroleum in long, colourless needles and melts at 82° . The *p-ester* is a yellow oil boiling at 195 — 205° ; the *acid* crystallises from alcohol in pale yellow flakes and melts at 134 — 135° .

T. M. L.

Formation of Chains. LI. Chloro- and Bromo-phenols. Summary of Quantitative Results on the Condensation of Phenols with Esters of α -Bromo-fatty Acids. By CARL A. BISCHOFF [and, in part, HERR, JENTSCHMEN, and SSYROTSCHKIN] (*Ber.*, 1900, 33, 1603—1611).—*Ethyl α -2:4-dichlorophenoxypropionate*, $\text{C}_6\text{H}_3\text{Cl}_2 \cdot \text{O} \cdot \text{CHMe} \cdot \text{CO}_2\text{Et}$, is a yellowish oil and boils at 173 — 176° under 12 mm. pressure; the *acid* crystallises from acetone in large prisms, and melts at 117 — 118° .

Ethyl α -2:4-dichlorophenoxyisobutyrate, $\text{C}_6\text{H}_3\text{Cl}_2 \cdot \text{O} \cdot \text{CMe}_2 \cdot \text{CO}_2\text{Et}$, is a colourless liquid with a faint odour; the *acid* did not solidify in 5 years.

Ethyl 2:4:6-trichlorophenoxyacetate, $\text{C}_6\text{H}_2\text{Cl}_3 \cdot \text{O} \cdot \text{CH}_2 \cdot \text{CO}_2\text{Et}$, crystallises from alcohol in needles and melts at 41° ; the *acid* crystallises from dilute alcohol in minute, felted, colourless needles and melts at 177° .

Ethyl 2:4:6-tribromophenoxyacetate crystallises from light petroleum in colourless needles and melts at 81° . The *acid* crystallises from dilute alcohol in needles and melts at 200° .

The paper contains a summary of all the quantitative measurements on the condensation of phenols with esters of the α -bromo-fatty acids, and the influence of the various substituting groups is discussed in detail.

T. M. L.

Catecholacetic Acid. By H. LUDEWIG (*J. pr. Chem.*, 1900, [ii], 61, 345—380).—The salts and a number of derivatives of catecholacetic acid (D. R.-P. 87,336) are described. The *methyl ester*, $\text{OH} \cdot \text{C}_6\text{H}_4 \cdot \text{O} \cdot \text{CH}_2 \cdot \text{CO}_2\text{Me}$, crystallises from light petroleum in long felted needles which melt at 59° , and contain rather more than $1\text{H}_2\text{O}$; the anhydrous ester is a colourless, hygroscopic oil which readily passes into the hydrated crystalline form. The *ethyl ester* crystallises from light petroleum in white tablets, melts at 53° , and on further heating loses alcohol and is converted into the lactone which begins to distil at 237° .

Acetylcatecholacetic acid, $\text{OAc} \cdot \text{C}_6\text{H}_4 \cdot \text{O} \cdot \text{CH}_2 \cdot \text{CO}_2\text{H}$, crystallises from benzene in small, white needles, melts at 110° and on heating is converted into acetic acid and the lactone.

Phosphorus trichloride converts the acid into the lactone and not into the acid chloride.

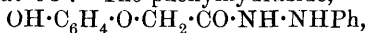
Catecholacetamide, $\text{OH} \cdot \text{C}_6\text{H}_4 \cdot \text{O} \cdot \text{CH}_2 \cdot \text{CO} \cdot \text{NH}_2$, prepared by heating

the ammonium salt formed by the action of alcoholic ammonia on the methyl ester or by the action of dry ammonia on an ethereal solution of the lactone, crystallises from alcohol in stout, colourless prisms, melts at 108° and contains $1\text{H}_2\text{O}$, but is converted by fusion into the anhydrous amide which crystallises from benzene and melts at 130° .

Catecholacetanilide crystallises from alcohol in long, silky needles, melts at 161° , and distils at 250° ; it gives no coloration with ferric

chloride and probably has the constitution $\text{C}_6\text{H}_4 \begin{matrix} \text{O}\cdot\text{CH}_2\cdot\text{CO} \\ \text{O} \text{---} \text{NH}_2\text{Ph} \end{matrix}$;

the *acetyl* derivative, $\text{OAc}\cdot\text{C}_6\text{H}_4\cdot\text{O}\cdot\text{CH}_2\cdot\text{CO}\cdot\text{NHPh}$, crystallises from benzene in minute, white needles and melts at 105° ; the *benzoyl* derivative crystallises from alcohol in long, white needles and melts at 117° . The *p-toluidide*, $\text{OH}\cdot\text{C}_6\text{H}_4\cdot\text{CO}\cdot\text{NH}\cdot\text{C}_7\text{H}_7$, crystallises from alcohol in white flakes and melts at 147° . The *o-toluidide* crystallises from benzene in white needles, melts at 105° , and distils at 220° . The *methylanilide*, $\text{OH}\cdot\text{C}_6\text{H}_4\cdot\text{CO}\cdot\text{NMePh}$, separates from ether in large, colourless, rhombic crystals and melts at 95° . The *piperidide*, $\text{OH}\cdot\text{C}_6\text{H}_4\cdot\text{CO}\cdot\text{C}_5\text{NH}_{10}$, crystallises from alcohol in large, colourless tablets and melts at 98° . The phenylhydrazide,



crystallises from alcohol in white, glistening flakes, melts at 191° , and is probably identical with the substance prepared by Moureu (Abstr., 1899, i, 125) by the action of phenylhydrazine acetate on catecholacetic acid.

Ethyl dinitrocatecholacetate, $\text{OH}\cdot\text{C}_6\text{H}_2(\text{NO}_2)_2\cdot\text{O}\cdot\text{CH}_2\cdot\text{CO}_2\text{Et}$, produced by the action of nitrous acid on an alcoholic solution of catechol acetic acid, crystallises from dilute alcohol in white, glistening flakes which melt at 88° and contain $1\text{H}_2\text{O}$, whilst the anhydrous ester is yellow and melts at 79° . In acetic acid solution, nitrous acid converts catecholacetic acid into dinitrocatecholacetic acid and then into oxalic acid.

Dinitrocatecholacetanilide, $\text{OH}\cdot\text{C}_6\text{H}_2(\text{NO}_2)_2\cdot\text{O}\cdot\text{CH}_2\cdot\text{CO}\cdot\text{NHPh}$, prepared by the action of nitrous acid on an alcoholic solution of catecholacetanilide, crystallises from alcohol in yellow, felted needles, and melts at 199° .

Nitrocatecholacetic acid, prepared by the action of nitric acid (1 mol.) on a solution of catecholacetic acid in acetic acid, crystallises from water in white, felted needles and melts at 183° . *Dinitrocatecholacetic acid*, prepared in a similar manner, crystallises from water in small, yellow needles which melt at 122° and contain $1\text{H}_2\text{O}$; the anhydrous acid separates from benzene in yellow crystals and melts at 147° .

Bromocatecholacetic acid, prepared by the action of bromine (1 mol.) on an ethereal solution of catecholacetic acid, crystallises from water in white needles and melts at 158° ; the *ethyl* ester crystallises from dilute alcohol in long, colourless prisms and melts at 48° . *Ethyl dibromocatecholacetate* crystallises from dilute alcohol in white tablets which melt at 89° and contain $\frac{1}{2}\text{H}_2\text{O}$; the anhydrous ester melts at 69° ; the *acid* crystallises from water in minute, white needles and melts at 158° ; the *lactone*, $\text{C}_6\text{H}_2\text{Br}_2 \begin{matrix} \text{O}\cdot\text{CH}_2 \\ \text{O}\cdot\text{CO} \end{matrix}$, crystallises from light petroleum and melts at 106° . *Ethyl tribromocatecholacetate* crystallises

in white flakes and melts at 118° . *Ethyl tetrabromocatecholacetate*, $\text{OH}\cdot\text{C}_6\text{Br}_4\cdot\text{O}\cdot\text{CH}_2\cdot\text{CO}_2\text{Et}$, crystallises from alcohol in minute, white needles and melts at 153° ; the *acid* separates from ether as a white powder and melts with decomposition at 231° . T. M. L.

Dichlorophthalic Acids: Products of Condensation. By ÉMILE C. SEVERIN (*Bull. Soc. Chim.*, 1900, [iii], 23, 374—382).—3:4-Dichloro-2'-dimethylaminobenzoylbenzoic acid and its derivatives have been already described (this vol., i, 296); when reduced with zinc and hydrochloric acid, this acid yields the corresponding 3:4'-dichloro-2'-dimethylaminobenzoylbenzoic acid, $\text{NMe}_2\cdot\text{C}_6\text{H}_4\cdot\text{CH}_2\cdot\text{C}_6\text{H}_2\text{Cl}_2\cdot\text{CO}_2\text{H}$, which crystallises in slender, white needles melting at 225° . N. L.

Formation of Chains. LII. Derivatives of Catechol. By CARL A. BISCHOFF (*Ber.*, 1900, 33, 1669—1676).—The quantitative results obtained by treating the disodium derivatives of catechol with the calculated quantity of ethyl α -bromopropionate, ethyl α -bromobutyrate, ethyl α -bromoisobutyrate, and ethyl α -bromoisovalerate are tabulated. *Diethyl catecho-bis- α -oxypropionate*, $\text{C}_6\text{H}_4(\text{O}\cdot\text{CHMe}\cdot\text{CO}_2\text{Et})_2$, is a yellow oil with a garlic-like odour and boils at 201° under 6 mm. pressure. *Catecho- α -oxypropionolactone*, obtained as a by-product in the preparation of the ethyl ester, crystallises in colourless plates melting at 51 — 51.5° ; when hydrolysed, these compounds yield two stereo-isomeric *catecho-bis- α -oxypropionic acids*, one of which crystallises in well-formed plates melting at 167 — 168° , and the other in aggregates of slender needles melting at 145.5 — 146° ; both acids, when distilled, yield the lactone and small quantities of lactic acid, and when treated with *p*-phenetidine yield *catecho-bis- α -oxypropionyl-*p*-diphenetide*, which crystallises in small, soft needles melting at 186 — 187° . *Catecho-bis- α -oxypropionic acid mono-*p*-phenetide* crystallises in large prisms melting at 169 — 170° , and *catecho-mono- α -oxypropionyl-*p*-phenetide* crystallises, with $2\text{H}_2\text{O}$, in large prisms melting at 163.5° .

Diethyl catecho-bis- α -oxybutyrate is a bright yellow oil which boils at 290 — 330° under 744 mm. pressure, and at 195 — 225° under 13 mm. pressure, and, when hydrolysed, yields an oily *acid*, which, when distilled, forms the *anhydride*, which is an oil boiling at 240 — 250° under 107 mm. pressure; *catecho-mono- α -oxybutyrolactone*, obtained as a by-product in the preparation of the ethyl ester, is a bright yellow oil which boils at 120 — 130° under 6 mm. pressure.

Diethyl catecho-bis- α -oxyisobutyrate is a bright yellow oil boiling at 197° under 27 mm. pressure; *catecho-mono- α -oxyisobutyrolactone* forms colourless crystals melting at 49.5 — 50.5° ; the ethyl ester, when hydrolysed, yields the oily *acid*, which boils at 224° under 24 mm. pressure, but is then partly converted into the *anhydride*, which crystallises in six-sided plates melting at 188 — 188.5° .

Diethyl catecho-bis- α -oxyisovalerate is a yellow oil which boils at 210 — 215° under 48 mm. pressure, and when hydrolysed yields the *anhydride*, which boils at 230 — 240° under 20 mm.; *catecho-mono- α -oxyisovalerolactone* is a bright, yellow oil, which boils at 250 — 260° under 753 mm. pressure.

R. H. P.

Formation of Chains. LIII. Derivatives of Resorcinol and Orcinol. By CARL A. BISCHOFF [and, in part, ABRAMSON, AGROZKIN, and MINSKI] (*Ber.*, 1900, **33**, 1676—1686).—Quantitative experiments with the disodium derivatives of resorcinol and orcinol analogous to those described in the preceding abstract are tabulated.

Diethyl resorcino-bis- α -oxypropionate is a thick, yellow oil which partly solidifies in the cold to needle-shaped crystals melting at 72.5° , boils at $202\text{--}204^\circ$ under 13 mm. pressure, and when hydrolysed yields the corresponding *acid*, which crystallises, with $1\frac{1}{2}\text{H}_2\text{O}$, in colourless, lustrous needles melting at 226° ; it is probable that both these are mixtures of stereoisomeric compounds.

Diethyl resorcino-bis- α -oxybutyrate is an oil boiling between 205° and 240° under 55 mm. pressure, and when hydrolysed yields the corresponding *acid*, which crystallises with $1\frac{1}{2}\text{H}_2\text{O}$, melts at 111° , boils at $220\text{--}230^\circ$ under 150 mm. pressure, and forms a *calcium* salt which is a yellow powder containing $3\text{H}_2\text{O}$.

Diethyl resorcino-bis- α -oxyisobutyrate is a bright yellow, viscous oil which boils at $208\text{--}209^\circ$ under 4 mm. pressure, and, when hydrolysed, yields an indefinite *acid*, which decomposes on distillation under reduced pressure.

Diethyl resorcino-bis- α -oxyisovalerate is a bright yellow oil, which boils at $200\text{--}206^\circ$ under 20 mm. pressure, and, when hydrolysed, yields the corresponding *acid*, which boils at $230\text{--}240^\circ$ under 85 mm. pressure.

Diethyl orcino-bis- α -oxypropionate, $\text{C}_6\text{H}_3\text{Me}(\text{O}\cdot\text{CHMe}\cdot\text{CO}_2\text{Et})_2$, is a yellow oil with a garlic-like odour, which boils at $314\text{--}317.5^\circ$ under 764 mm. pressure, and, when hydrolysed, yields the corresponding *acid*, which sinters at 137° and melts at 146° .

Diethyl orcino-bis- α -oxybutyrate is a yellow oil which boils at $330\text{--}340^\circ$ under 763 mm. pressure, and when hydrolysed yields the corresponding *acid*, which is an oil.

The condensation of disodium orcinoxide and diethyl α -bromoisobutyrate yields an indefinite *compound*, which boils at $280\text{--}300^\circ$ under 761 mm. pressure, and, when hydrolysed, yields an oily *acid*. The corresponding *compound* derived from diethyl α -bromoisovalerate is a yellow oil which boils at $310\text{--}315^\circ$ under 764 mm. pressure, and when hydrolysed yields an oily *acid*.

R. H. P.

Formation of Chains. LIV. Derivatives of Quinol. By CARL A. BISCHOFF [and, in part, OLZEWSKI, BASSEWICZ, STIELMANN, and DUNIN-SULGUSTOWSKI] (*Ber.*, 1900, **33**, 1686—1692).—Quantitative experiments with disodium quinol, similar to those described in the two preceding abstracts, are tabulated.

Diethyl quino-bis- α -oxypropionate, $\text{C}_6\text{H}_4(\text{O}\cdot\text{CHMe}\cdot\text{CO}_2\text{Et})_2$, occurs in two isomeric forms, one of which forms large, colourless crystals melting at $91\text{--}91.5^\circ$, and when hydrolysed yields an *acid* melting at 235° , whilst the other is an oil which boils at $187\text{--}190^\circ$ under 6 mm. pressure, and when hydrolysed yields an isomeric *acid* melting at $220\text{--}224^\circ$.

Diethyl quino-bis- α -oxybutyrate was obtained as a viscous, bright yellow oil, which could be divided, when distilled, into two fractions

boiling at 210—212° and 212—217° under 10 mm. pressure; the lower fraction, when hydrolysed, yields an *acid* which crystallises in prisms melting at 198—199°, and the higher fraction an *acid* which is an oil.

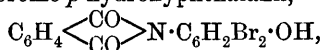
Diethyl quino-bis-α-oxyisobutyrate crystallises in long needles melting at 81°, and when hydrolysed yields the corresponding *acid*, which crystallises in long, thin, colourless plates melting at 189°.

Diethyl quino-bis-α-oxyisovalerate is a bright yellow oil which boils at 210—215° under 20 mm. pressure, and when hydrolysed yields the corresponding *acid*, which forms plate-shaped crystals melting at 209°.

The paper concludes with a comparison between the various dihydroxybenzenes, which shows that the para-position is best suited to these condensations, and the ortho-position least.

R. H. P.

Tetrabromophenolphthalein. By HANS MEYER (*Monatsh.*, 1900 21, 263—266).—Dibromo-*p*-hydroxyphthalanil,

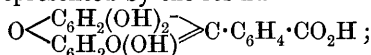


which is formed in small quantity during the production of Friedländer and Stange's tetrabromophenolphthaleinoxime (compare Abstr., 1893, i, 719) becomes the chief product if the proportion of hydroxylamine hydrochloride is increased, or when the oxime is further treated with this reagent. It crystallises in long, slender, colourless needles, is slightly soluble in alcohol, chloroform, or glacial acetic acid, and freely soluble in alkali carbonates or hydroxides. The solution in ammonia becomes blood-red on standing and darkens later. Hydrochloric acid decomposes it, although with difficulty, into phthalic acid and dibromo-aminophenol (compare Abstr., 1899, i, 707). The substance was synthesised by brominating the product of the condensation of phthalic anhydride with *p*-aminophenol. Tetrabromophenolphthalein, which, like the unbrominated phthalein, forms a stable oxime with excess of hydroxylamine hydrochloride, yields phthalimide, if there is no excess (compare Posner's *o*-cyanobenzaldoxime, Abstr., 1897, i, 472).

R. L. J.

Gallein and Cœrulein. By WILLIAM R. ORNDORFF and C. E. BREWER (*Amer. Chem. J.*, 1900, 23, 425—431).—Gallein is the phthalein of pyrogallol, as stated by von Baeyer (*Ber.*, 1871, 4, 663), whilst gallin is the corresponding phthalin.

Gallein is best represented by the formula



it yields a methyl and an ethyl ester, and a triphenylcarbamate, and also gives coloured tetramethyl and tetraethyl ethers which are easily hydrolysed by solution of sodium carbonate. It also reacts in the tautomeric lactoid form, $\text{O} \begin{array}{c} \diagup \text{C}_6\text{H}_2(\text{OH})_2 \\ \diagdown \text{C}_6\text{H}_2\text{O}(\text{OH})_2 \end{array} \text{C} \begin{array}{c} \diagup \text{O} \\ \diagdown \text{C}_6\text{H}_4 \end{array} \text{CO}$, since it forms a colourless tetracetate, tetrabenzoate, and tetraphenylsulphonate, and also colourless tetramethyl and tetraethyl ethers. The colourless trimethyl ether closely resembles phenolphthalein; it dissolves in sodium carbonate or sodium hydroxide, forming a red solution from which it is precipitated colourless by acids; acetic anhydride converts

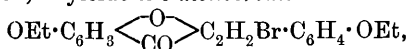
it into a colourless acetate which is insoluble in alkalis. The same colourless trimethyl ether results from the hydrolysis of the coloured tetramethyl ether.

Buchka (Abstr., 1882, 59), has stated that when gallein is reduced it yields hydrogallein, which, on further reduction is converted first into gallin, and finally into gallol. Some doubt was cast on the accuracy of these conclusions by the observations of Herzig (Abstr., 1892, 1319), who was unable to obtain hydrogallein. The present authors find that hydrogallein does not exist, that Buchka's gallol is really gallin, and that his hydrogallein, gallin, and gallol acetates are identical in every respect.

Gallin yields a colourless tetracetate which furnishes a silver salt, and a pentamethyl ether which has no acid properties and is easily hydrolysed; its constitution is best expressed by the formula
$$\text{O} \begin{array}{c} \diagup \text{C}_6\text{H}_2(\text{OH})_2 \diagdown \\ \diagdown \text{C}_6\text{H}_2(\text{OH})_2 \diagup \end{array} \text{CH} \cdot \text{C}_6\text{H}_4 \cdot \text{CO}_2\text{H}.$$
 Cærulein is best represented by the formula
$$\text{CO} - \text{C}_6\text{H}_4 - \text{C} \begin{array}{c} \diagup \text{C}_6\text{H}_2\text{O}(\text{OH}) \diagdown \\ \diagdown \text{C}_6\text{H}(\text{OH})_2 \diagup \end{array} \text{O};$$
 it gives a triacetate which is easily reduced with zinc dust and acetic acid. Cærolin yields a pentacetate, but not a tetracetate as stated by Buchka (*loc. cit.*); its constitution may be expressed by the formula
$$\text{OH} \cdot \text{C} \begin{array}{c} \diagup \text{C}_6\text{H}_4 - \text{C} \cdot \text{C}_6\text{H}_2(\text{OH})_2 \diagdown \\ \diagdown \text{C}_6\text{H}(\text{OH})_2 \diagup \end{array} \text{O}.$$

E. G.

6:3'-Dihydroxyflavone. By J. BLUMSTEIN and STANISLAUS VON KOSTANECKI (*Ber.*, 1900, 33, 1478—1483).—6:3'-*Diethoxyflavanone*,
$$\text{OEt} \cdot \text{C}_6\text{H}_3 \begin{array}{c} \diagup \text{O} - \text{CH} \cdot \text{C}_6\text{H}_4 \cdot \text{OEt} \\ \diagdown \text{CO} - \text{CH}_2 \end{array}$$
, obtained by the condensation of *m*-ethoxybenzaldehyde with 2-hydroxy-5-ethoxyacetophenone under conditions previously described (compare this vol., i, 237, 238), crystallises from alcohol in colourless needles, melts at 96—97°, and has a blue fluorescence in alcoholic solution; with bromine in carbon disulphide solution, it yields the *monobromo*-derivative,

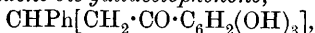


which crystallises from alcohol in white needles, melts at 112—113°, and loses hydrogen bromide when treated with warm concentrated alcoholic potassium hydroxide, forming 6:3'-*diethoxyflavone*,

$$\text{OEt} \cdot \text{C}_6\text{H}_3 \begin{array}{c} \diagup \text{O} - \text{C} \cdot \text{C}_6\text{H}_4 \cdot \text{OEt} \\ \diagdown \text{CO} - \text{CH} \end{array}$$
 This crystallises from alcohol in white leaflets, melts at 135—136°, shows a greenish fluorescence in sulphuric acid solution, and is resolved by heating with sodium in alcoholic solution, into 2-hydroxy-5-ethoxyacetophenone and *m*-ethoxybenzoic acid; when boiled for several hours with concentrated hydriodic acid, it yields 6:3'-*dihydroxyflavone*, which crystallises from alcohol in short, thick, colourless needles and melts at 300°; 6:3'-*diacetoxyflavone* crystallises from alcohol in white needles and melts at 169—170°.

Resacetophenone monoethyl ether (2 mols.) condenses with benzaldehyde in alcoholic solution under the influence of hydrogen chloride to form, not a flavanone, but *benzylidene-bis-resacetophenone monoethyl*

ether, $\text{CHPh}[\text{CH}_2 \cdot \text{CO} \cdot \text{C}_6\text{H}_3(\text{OH}) \cdot \text{OEt}]_2$, $[\text{CO} : \text{OH} : \text{OEt} = 1 : 2 : 4]$; this crystallises from alcohol in slightly yellow needles, melts at 211° , and yields a *diacetate* which forms small, white needles and melts at $138-139^\circ$. *Benzylidene-bis-gallacetophenone*,



obtained similarly, crystallises, with $2\text{H}_2\text{O}$, from dilute alcohol in beautiful rosettes of needles which lose their water of crystallisation when kept in a desiccator, and become opaque; it melts at 226° , and yields a *hexacetyl* derivative which crystallises from alcohol and melts at $171-172^\circ$.

W. A. D.

Oximes of some Flavonones. By STANISLAUS VON KOSTANECKI (*Ber.*, 1900, 33, 1483-1484).—Although the flavones, like the xanthenes, are indifferent to hydroxylamine, the flavonones readily form oximes.

6-Ethoxyflavanoneoxime, $\text{OEt} \cdot \text{C}_6\text{H}_3 \begin{smallmatrix} \text{O} \text{---} \text{CHPh} \\ \text{C}(\text{N} \cdot \text{OH}) \cdot \text{CH}_2 \end{smallmatrix}$, crystallises from alcohol in white needles and melts at $185-186^\circ$.

4'-Methoxy-6-ethoxyflavanone, $\text{OEt} \cdot \text{C}_6\text{H}_3 \begin{smallmatrix} \text{O} \text{---} \text{CH} \cdot \text{C}_6\text{H}_4 \cdot \text{OMe} \\ \text{C}(\text{N} \cdot \text{OH}) \cdot \text{CH}_2 \end{smallmatrix}$, crystallises from alcohol in white needles and melts at $190-191^\circ$; it is hydrolysed by boiling with alcoholic hydrochloric acid. The *acetate* crystallises from alcohol in white needles and melts at 168° .

T. M. L.

7-Acetylamino- β -naphthaquinone. By FRIEDRICH KEHRMANN and H. WOLFF (*Ber.*, 1900, 33, 1538-1542).—*7-Acetylamino-2-naphthol*, $\text{NHAc} \cdot \text{C}_{10}\text{H}_6 \cdot \text{OH}$, obtained by shaking 7-amino-2-naphthol with acetic anhydride and a little dry sodium acetate, crystallises from alcohol in colourless, glistening plates melting at 220° ; on treatment with nitrous acid, it yields a *nitroso*-derivative, probably with the oxime constitution $\text{NHAc} \cdot \text{C}_{10}\text{H}_5 \cdot \text{O} \cdot \text{N} \cdot \text{OH}$; this crystallises from benzene in yellowish-red, glistening plates decomposing at about 220° , and dissolves readily in boiling water, alcohol, or acetic acid. Dilute sulphuric acid precipitates it from its solution in alkalis as a dark red, crystalline precipitate which slowly changes to a pale yellow powder. When reduced with stannous chloride, the oxime yields *acetyldiamino-naphthol*, $\text{NHAc} \cdot \text{C}_{10}\text{H}_5(\text{OH}) \cdot \text{NH}_2$ $[\text{NH}_2 : \text{OH} : \text{NHAc} = 1 : 2 : 7]$, in the form of its *hydrochloride*, together with a certain amount of diamino-naphthol hydrochloride, the *diacetyl* derivative of which crystallises in colourless needles melting at 226° .

7-Acetylamino-1:2-naphthaquinone crystallises from alcohol in glistening, almost black, needles, which rub down to a dark red powder; it melts and decomposes at about 224° , and is soluble in alcohol, acetic acid, or boiling water, yielding blood-red solutions. It differs from the isomeric compound previously described (*Abstr.*, 1899, i, 81) in its much deeper colour. When treated with amines, the hydrogen atom in position 4 is readily replaced by amino-groups.

7-Acetylamino-4-anilino- β -naphthaquinone, $\text{NHAc} \cdot \text{C}_{10}\text{H}_4\text{O}_2 \cdot \text{NHPH}$, forms small, brownish-red crystals, melts and decomposes at about 280° , and dissolves in alkalis, boiling alcohol, or acetic acid.

9-Acetylaminonaphthaphenazine, $\text{NHAc} \cdot \text{C}_{10}\text{H}_5 \begin{smallmatrix} \text{N} \\ \diagup \quad \diagdown \\ \text{N} \end{smallmatrix} \text{C}_6\text{H}_4$, obtained by the condensation of *o*-phenylenediamine hydrochloride and 7-acetylaminonaphthaquinone in the presence of alcohol and a few drops of dilute sulphuric acid, crystallises from alcohol in yellow needles melting at 288° ; its alcoholic solution possesses a slight green fluorescence. When hydrolysed with sulphuric acid, it yields 9-aminonaphthaphenazine, which crystallises from alcohol in glistening, reddish-brown needles melting at 232° , insoluble in water, and yielding mono-acid salts which have an olive-green colour. J. J. S.

Preparation of Dialkylaminodichloroanthraquinones. By ÉMILE C. SEVERIN (*Compt. rend.*, 1900, 130, 1405—1407).—2-Dimethylamino-3:4-dichlorobenzylbenzoic acid, obtained by reduction of the corresponding benzoylbenzoic acid (this vol., i, 296), is a white solid which melts at 233° and becomes yellow when exposed to air (compare, however, this vol., i, 445). The corresponding diethylamino-acid crystallises in white needles melting at 237° . When heated with concentrated sulphuric acid at 66° , these acids yield respectively 2-dimethylamino-5:6-dichloroanthraquinone, which crystallises in bronzed red needles melting at 188° , and the diethylamino-compound, which is similar in appearance, but melts at 175° . In this condensation, the benzylbenzoic acid is first converted into a ketohydroanthracene, which is subsequently oxidised by the excess of sulphuric acid.

The corresponding benzoylbenzoic acids, however, do not undergo similar condensation, which seems to be prevented by the presence of the two chlorine atoms in the 3 and 4 positions with respect to the carboxyl groups. C. H. B.

New Homologues of Alizarin, Hystazarin, and Quinizarin. By STEFAN VON NIEMENTOWSKI (*Ber.*, 1900, 33, 1629—1636).—When 4-methylphthalic anhydride is heated with catechol (1 mol.) and concentrated sulphuric acid for several hours at 185° , 2-methyl-6:7-hystazarin, $\text{C}_6\text{H}_3\text{Me} \begin{smallmatrix} \text{CO} \\ \diagup \quad \diagdown \\ \text{CO} \end{smallmatrix} \text{C}_6\text{H}_2(\text{OH})_2$, is formed together with a smaller proportion of the isomeric methylalizarin $[(\text{OH})_2 : \text{Me} = 1 : 2 : 6 \text{ or } 1 : 2 : 7]$. The latter crystallises from benzene, in which it is moderately soluble, in orange-red needles, melts at 216° , and can be sublimed; its tinctorial properties and absorption spectrum are similar to those of alizarin; its diacetyl derivative, $\text{C}_{19}\text{H}_{14}\text{O}_6$, crystallises from alcohol in stellar aggregates of bright yellow needles, and melts, with previous softening, at 176° . 2-Methyl-6:7-hystazarin is almost insoluble in benzene, but separates from alcohol or glacial acetic acid in yellow crystals which melt and decompose between 320° and 340° , and, when distilled with zinc dust in a stream of hydrogen, yield 2-methylanthracene; the diacetate, $\text{C}_{19}\text{H}_{14}\text{O}_6$, crystallises from alcohol in straw-coloured, felted needles and melts at 208° .

2-Methyl-5:8-quinizarin, prepared by heating quinol with 4-methylphthalic anhydride (1 mol.) and concentrated sulphuric acid for 5—10 hours at 140 — 160° , crystallises from a mixture of alcohol and benzene in lustrous, orange-gold leaflets, and melts at 165° ; after fusion and resolidification, or after sublimation, however, it melts at 175° .

The *diacetyl* derivative crystallises from alcohol in yellow, obliquely truncated plates and melts at 204° ; attempts to prepare the corresponding dibenzoyl derivative failed.

W. A. D.

Bromine Derivatives of Quinizarin. By CARL LIEBERMANN and C. N. RIIBER (*Ber.*, 1900, 33, 1658—1664).—*Bromoquinizarin*,

$C_6H_4 \begin{smallmatrix} \diagup CO \\ \diagdown CO \end{smallmatrix} C_6HBr(OH)_2$, obtained when quinizarin is dissolved in 25 times its weight of glacial acetic acid and then boiled for 12 hours with 3 times its weight of bromine, forms a red, crystalline powder insoluble in all ordinary organic solvents, but soluble in alkali hydroxides, yielding blue or bluish-violet solutions. It sublimes at about 300° under reduced pressure and is deposited as ruby-red, glistening needles or plates.

Dibromoquinizarin, $C_6H_4 \begin{smallmatrix} \diagup CO \\ \diagdown CO \end{smallmatrix} C_6Br_2(OH)_2$, formed when quinizarin is heated with 6 times its weight of dry bromine in sealed tubes at 100° for 8 hours, sublimes at about 350° under reduced pressure, yielding red needles, and appears to form an unstable compound with bromine, which is, however, decomposed on exposure to the air. It is somewhat sparingly soluble in potassium hydroxide, yielding a deep blue solution, but is insoluble in cold sodium carbonate solution and in most organic solvents. The blue alkaline solution and the red solution in concentrated sulphuric acid exhibit two absorption bands almost identical with those given by similar solutions of quinizarin itself. When fused with potash, it yields purpurin and probably hydroxypurpurin which on oxidation are converted into phthalic acid.

A mixture of two isomeric *hexabromides*, $C_{14}H_8O_4Br_6$, is obtained when quinizarin is left in contact with some 40 times its weight of bromine for 3 days at 0° . The two may be separated by the aid of a moderate amount of carbon disulphide in which the one is insoluble; when the filtrate is cooled and mixed with its own volume of light petroleum, brownish-yellow crystals of the more soluble isomeride having the composition $2C_{14}H_8O_4Br_6 \cdot CS_2$ are obtained. The less soluble compound forms canary yellow crystals, and when heated to 210 — 220° melts and decomposes, yielding bromine, hydrogen bromide, and bromoquinizarin. It is insoluble in cold sodium carbonate and only sparingly soluble in ammonia, but more readily in potassium hydroxide, yielding a yellow solution.

The more soluble compound loses its carbon disulphide at 70° under reduced pressure and decomposes at 175° in much the same manner as its isomeride.

Bromoquinizarin dibromide, $C_{14}H_7BrO_4Br_2$, obtained by the action of an excess of bromine on quinizarin at 40 — 50° , forms reddish-brown crystals decomposing at 210° and soluble in carbon disulphide, benzene, or acetic acid, but insoluble in cold alkalis. Bromoalizarin appears to combine with 2 mols. of bromine at 0° , but this bromine is readily given up again at the ordinary temperature.

J. J. S.

Action of Hydrogen Bromide on Dextrorotatory Benzylidenecamphor, Bromobenzylcamphor and Dextrorotatory Benzylidenecampholic and Phenylhydroxyhomocampholic Acids. By ALBIN HALLER and JULES MINGUIN (*Compt. rend.*, 1900, 130, 1362—1366).—*Bromobenzylcamphor*, $C_8H_{14} \begin{smallmatrix} \text{CH} \cdot \text{CHPhBr} \\ \text{CO} \end{smallmatrix}$, obtained

by the prolonged action of an acetic acid solution of hydrogen bromide on benzylidenecamphor, crystallises from ether or light petroleum in white granules which melt at 146° . In alcoholic solution, it has $[\alpha]_D + 53.3^\circ$. If the benzylidenecamphor is heated with the acid solution at 100° under pressure, or if the bromo-derivative just described is treated in the same way, *phenylhydroxyhomocampholic acid*, $OH \cdot \text{CHPh} \cdot \text{CH}_2 \cdot C_8H_{14} \cdot \text{CO}_2H$, is obtained, together with a small quantity of a viscous *benzylidenecampholic acid*, $\text{CHPh} \cdot \text{CH} \cdot C_8H_{14} \cdot \text{CO}_2H$. If the bromobenzylcamphor is treated with alcoholic potash, the second acid is the main product, and the first is formed in small quantity.

Phenylhydroxyhomocampholic acid melts at 217° , in alcoholic solution, has $[\alpha]_D + 68.6^\circ$, and crystallises with 1 mol. alcohol in transparent, efflorescent prisms. The methyl ester prepared from the silver salt melts at 105° , and when dissolved in toluene has $[\alpha]_D + 66.4^\circ$. When heated with methyl alcohol and hydrochloric acid, this acid yields the methyl ester of the benzylidenecampholic acid, which boils at $205\text{--}210^\circ$ under 15 mm. pressure, and when dissolved in toluene has $[\alpha]_D + 22^\circ$.

The authors attribute to the influence of the double bond of the CHR group the readiness with which the benzylidene camphor combines with the elements of water, whilst the benzylidenecampholic acid is probably formed simply by the dehydration of the phenylhydroxyhomocampholic acid. The low rotatory power of benzylidenecampholic acid, as compared with that of benzylidenecamphor, is noteworthy, and indicates that a double bond on one of the branches of a broken camphor chain does not increase the rotatory power of the new product.

C. H. B.

Rhodinol and Citronellol. By LOUIS BOUVEAULT (*Bull. Soc. Chim.*, 1900, [iii], 23, 458—463).—The author briefly reviews the history of rhodinol and citronellol, replies to the criticisms of Tiemann and Schmidt (*Abstr.*, 1896, i, 382), and maintains the accuracy of Barbier and Bouveault's views (*Abstr.*, 1896, i, 446, 491, 492; 1897, i, 537) as to the constitution and distinct individuality of these compounds.

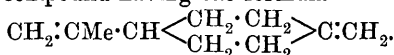
N. L.

Transformation of Rhodinal into Menthone. By LOUIS BOUVEAULT (*Bull. Soc. Chim.*, 1900, [iii], 23, 463—466).—A reply to Tiemann and Schmidt (*Abstr.*, 1897, i, 199). Analyses are quoted in further proof of the isomeric change of rhodinal into menthone described by Barbier and Bouveault (*Abstr.*, 1896, i, 491).

N. L.

Pseudo- and Ortho series of Terpenes, Terpene-alcohols, and Terpene-ketones. By FRIEDRICH W. SEMMLER (*Ber.*, 1900, 33, 1455—1467).—Terpene derivatives which contain a double bond between the nucleus and the side chain are termed by the author

pseudo-derivatives, the isomeric substances containing the double bond in the nucleus being denoted as *ortho*-derivatives; thus limonene, $\text{CH}_2:\text{CMe}\cdot\text{CH}\left\langle\begin{smallmatrix}\text{CH}_2\cdot\text{CH} \\ \text{CH}_2\cdot\text{CH}_2\end{smallmatrix}\right\rangle\text{CMe}$, would be an *ortho*-terpene, the corresponding *pseudo*-compound having the formula

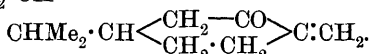


It is not improbable that dipentene has the latter formula, instead of being, as usually assumed, [*d* + *l*]-limonene; both substances would give rise to the same derivatives on interaction with halogen acids.

Orthopinene would be $\text{CH}_2\left\langle\begin{smallmatrix}\text{CH}—\text{CH}_2 \\ \text{CH}—\text{CMe}\end{smallmatrix}\right\rangle\text{CH}$, and ψ -pinene

$\text{CH}_2\left\langle\begin{smallmatrix}\text{CH}—\text{CH}_2 \\ \text{CH}—\text{CMe}_2\end{smallmatrix}\right\rangle\text{C}\cdot\text{CH}_2$; orthocarvone would have the formula

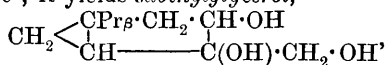
$\text{CHMe}_2\cdot\text{CH}\left\langle\begin{smallmatrix}\text{CH}_2\cdot\text{CO} \\ \text{CH}_2\cdot\text{CH}\end{smallmatrix}\right\rangle\text{CMe}$, and ψ -carvone the formula



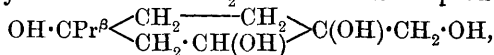
Sabinol, isolated by Fromm's method (Abstr., 1898, i, 674) from oil of savin, has a sp. gr. 0.9432 at 20°, μ_D 1.488, and a molecular refraction 46.5; from the following facts, it appears to be a ψ -terpene-

alcohol, $\text{CH}_2\left\langle\begin{smallmatrix}\text{CPr}^\beta\cdot\text{CH}_2\cdot\text{CH}\cdot\text{OH} \\ \text{CH}—\text{C}\cdot\text{CH}_2\end{smallmatrix}\right\rangle$. It is not a tertiary alcohol, since

it does not lose oxygen when heated with zinc dust (compare Abstr., 1894, i, 611; and this vol., i, 351), and because of the shape of the curves obtained by molecular weight determinations; it is not a primary alcohol, since it fails to interact with phthalic anhydride (compare Stephan, Abstr., 1899, i, 921). Hence, by exclusion, it is a secondary alcohol, although attempts to oxidise it to the corresponding ketone, $\text{C}_{10}\text{H}_{14}\text{O}$, failed. When oxidised with aqueous potassium permanganate at 0°, it yields *sabinylglycerol*,



which crystallises from water, melts at 152–153°, and is converted, on warming with water containing a trace of acid, into cuminyl alcohol; this occurs by the addition of $1\text{H}_2\text{O}$ to form the compound



and the subsequent loss of $2\text{H}_2\text{O}$. When further oxidised by potassium permanganate, sabinol yields tanacetonedicarboxylic acid,

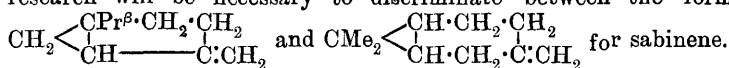
$\text{CH}_2\left\langle\begin{smallmatrix}\text{CPr}^\beta\cdot\text{CH}_2\cdot\text{CO}_2\text{H} \\ \text{CH}\cdot\text{CO}_2\text{H}\end{smallmatrix}\right\rangle$ (compare this vol., i, 240); on reduction with

sodium and amyl alcohol, it gives rise to tanacetyl alcohol, $\text{C}_{10}\text{H}_{18}\text{O}$, which is readily oxidised to tanacetone, characterised by its oxime (m. p. 52°). Sabinol is also converted into tanacetone by distilling with zinc dust, and, when warmed with absolute alcohol containing a few drops of sulphuric acid, yields cymene.

When oil of savin is distilled, a fraction, forming 30 per cent. of

the whole, boils between 162° and 170° , and consists principally of a terpene, $C_{10}H_{16}$, which the author terms *sabinene*; this has a sp. gr. 0.84, μ_D 1.466, a molecular refraction 44.9, and yields an oily *di-bromide* of sp. gr. 1.50. With ice-cold, aqueous potassium permanganate, sabinene yields a *glycol*, $C_{10}H_{18}O_2$, which boils at $148-150^{\circ}$ under 15 mm. pressure, crystallises from water, melts at 54° , and has a sp. gr. 1.021, μ_D 1.402, and a molecular refraction 47.41, the calculated value being 47.97; on warming with acidified water, the glycol yields a *dihydrocuminyl alcohol*, $C_{10}H_{16}O$, which boils at 242° , has a sp. gr. 0.9572, μ_D 1.5018, a molecular refraction 46.80 (that calculated for 2 ethylenoid linkings being 46.76), and is oxidised by chromic acid to cuminyl alcohol and cuminaldehyde. These facts indicate that one of the hydroxyl groups of the glycol is in the nucleus, and that in sabinene, as in sabinol, there is a double-bond from the nucleus to a methylene group. *Sabinenic acid*, $C_{10}H_{16}O_3$, formed along with the foregoing glycol, crystallises from water, melts at 57° , and yields a sparingly soluble, crystalline *sodium salt*; it is an α -hydroxy-acid, since it loses carbon dioxide when oxidised by lead peroxide to form *sabinene ketone*, $C_9H_{14}O$, which boils at 213° , has a sp. gr. 0.945, μ_D 1.4629, a molecular refraction 40.26 (that calculated for a ketone, $C_9H_{14}O$, without a double linking being 39.51), and yields a *semi-carbazone* crystallising from alcohol and melting at $135-137^{\circ}$. The ketone is laevorotatory (α_D in a 10 mm. tube = -18°), although sabinene, sabineneglycol, and sabinenic acid are all dextrorotatory.

On distilling sabinenic acid in a vacuum, water and hydrogen are eliminated and cumic acid formed (m. p. $117-118^{\circ}$). Additional research will be necessary to discriminate between the formulæ



W. A. D.

Essential Oil of Jasmine Blossom. IV. By ALBERT HESSE (*Ber.*, 1900, 33, 1585—1591. Compare Abstr., 1899, i, 376 and 441; and 1900, i, 48).—The investigation has been extended to the 'jasmine pur' obtained by extracting the blossom with a volatile solvent; of this, only about 25 per cent. is volatile with steam, and 5600 kilograms of blossom are therefore required to produce 1 kilogram of volatile oil. Where the oil is extracted from the blossoms by cold fat, only about 1000 kilograms are required, and the conclusion is therefore drawn that the blossoms only contain a small proportion of the oil ready formed, but steadily produce it during the 'enfleurage.' The oil differs in sp. gr. and in the proportion of ester from that obtained by 'enfleurage,' showing that the composition changes steadily after the blossoms are plucked.

'Jasmine pur' contains no methyl anthranilate, and therefore is not fluorescent. Jasnone is present, although the quantity was not sufficient for isolation, but there is not the slightest trace of indole, and this is therefore entirely absent in the blossoms, and is only produced during the 'enfleurage.'

T. M. L.

Precipitation of Dyes by Ammonium Persulphate. By FR. PROSCHER (*Chem. Zeit.*, 1900, 24, 262).—The following dyes are

quantitatively precipitated by the aid of ammonium persulphate: resorcinol-orange, neutral red, diethyltoluthionin chloride, succinicin-rhodamine, nitropentamethyl-violet, acridine-orange, and induline-scarlet; and the following almost completely: tetraethylsaffranine, Nile-blue; diethylsaffranine, thioflavine, rosinduline sulphate, phenosaffranine, chrysaniline, naphthol-blue, and thionine. The fact that the dyes are not oxidised may be due to their quinonoid structure. Methylene-green is, however, readily oxidised. J. J. S.

Leucomethylene-Blue. By GEORG COHN (*Ber.*, 1900, 33, 1567—1568).—Leucomethylene-blue is so unstable that the preparation of acyl derivatives is a matter of great difficulty. Its compound with zinc chloride, on the other hand, readily yields acyl derivatives when treated with an acyl chloride or anhydride in presence of pyridine. *Benzoyl-leucomethylene-blue* forms colourless crystals melting at 185—187°, and is stable in the air; its *picrate* melts at 178°. When treated with ferric chloride, it gives first a green coloration and then a precipitate of the blue colouring matter. *Anisyl-leucomethylene-blue* melts at 106—107°, and *propionyl-leucomethylene-blue* at 145—146°; *butyryl-leucomethylene-blue* is a yellowish, crystalline powder melting at 143°, and *valeryl-leucomethylene-blue* melts at 155—156°.

The compound with stannic chloride may be employed in a similar manner, and analogous compounds can be prepared from ethylene-blue and "new methylene-blue." A. H.

New Colouring Matters of Acid Function. By MAURICE PRUD'HOMME (*Bull. Soc. Chim.*, 1900, [iii], 23, 456—457).—The simultaneous methylation and sulphonation of amino-groups in certain colouring matters, leuco-bases, and chromogens may be brought about by heating with a mixture of sodium hydrogen sulphite and formaldehyde in acid solution. The application of this process to magenta, *p*-nitrodiaminotriphenylmethane, thionine, saffranine, and the nitranilines is referred to in the paper. N. L.

New Blue Colouring Matter, Fast to Alkalis. By MAURICE PRUD'HOMME (*Bull. Soc. Chim.*, 1900, [iii], 23, 457—458).—The action of formaldehyde and sodium hydrogen sulphite (see preceding abstract) on tetramethyltriaminodiphenyltolylmethane leads to the formation of a blue colouring matter in which the group $\text{NH}\cdot\text{CH}_2\cdot\text{SO}_3\text{H}$ stands in the *ortho*-position with respect to the central carbon atom; it resembles the similar *ortho*-sulphonated compounds prepared by Suais and Sandmeyer in resisting the action of alkalis. N. L.

Brilliant Fast Red G. By E. KOHNER (*J. pr. Chem.*, 1900, [ii], 61, 228—232).—"Brilliant fast red G" can be synthetically prepared by diazotising α -naphthylamine-5-sulphonic acid and subsequent treatment with β -naphthol.

α -Naphthylamine-5-sulphonic acid is the only α -naphthylaminesulphonic acid which gives a violet-red coloration with bromine water.

R. H. P.

Pilocarpine. By ADOLF PINNER and E. KOHLHAMMER (*Ber.*, 1900, 33, 1424—1431. Compare Jowett, *Trans.*, 1900, 77, 494, 851).—The observations of Hardy and Calmels (*Abstr.*, 1886, 724, 900, 1048; 1887, 1057) seem quite erroneous. No pyridinelactic acid could be obtained by prolonged boiling of pilocarpine with water or aqueous barium hydroxide; the alkali remained unchanged. Nor was it possible to obtain pyridinetartronic acid by oxidising pilocarpine with potassium permanganate; indeed, it seems possible that the product may be an acid free from nitrogen.

When pilocarpine is treated with three times its weight of bromine, 80 per cent. acetic acid being used as the solvent, yellowish-red needles of a perbromide, $C_{11}H_{14}O_2N_2Br_3 \cdot HBr \cdot Br_2$, are obtained; these melt at 106° (compare Chastaing, *Abstr.*, 1884, 468); the substance is not affected by water in the cold, however. When the perbromide is treated with dilute ammonia, dibromopilocarpine, $C_{11}H_{14}O_2N_2Br_2$, is formed; this was obtained crystalline and melted at 79° . By heating pilocarpine, $C_{11}H_{16}O_2N_2$, with bromine and water at 100° , *bromocarpic acid*, $C_{10}H_{15}O_4N_2Br$, is formed, along with another acid; evidently, the reaction is in a greater degree one of oxidation than of substitution. Bromocarpic acid melts at 194° ; its *barium* salt has the composition $C_{10}H_{13}O_4N_2BrBa \cdot 5H_2O$; when heated with strong aqueous barium hydroxide for 12 hours at 160 — 180° , the acid is for the most part entirely decomposed, and 78 per cent. of its nitrogen is obtained in the form of ammonia and methylamine. When pilocarpine is oxidised with permanganate, only 5 atoms of the latter per mol. of the alkaloid are taken up in the cold; probably, therefore, the bromine first oxidises the pilocarpine to a hydroxycarpic acid, $C_{11}H_{16}O_2N_2 + 5O = CO_2 + C_{10}H_{16}O_5N_2$, of which the hydroxyl group is then replaced by bromine through the agency of the hydrobromic acid formed in the first reaction.

C. F. B.

Pyridine Series. II. By WILHELM MARCKWALD, W. KLEMM, and H. TRABERT (*Ber.*, 1900, 33, 1556—1566. Compare *Abstr.*, 1894, i, 381).—2-Pyridyl mercaptan, $C_5NH_4 \cdot SH$, is formed by the action of potassium hydrosulphide on 2-chloropyridine, and crystallises in almost odourless, yellow prisms melting at 125° . Solutions of this substance in indifferent solvents and in dilute acids are yellow, whilst solutions in alkalis and strong acids are colourless. This is probably due to the fact that the substance is tautomeric, existing in the yellow form as a thiopyridone, $NH \begin{smallmatrix} \text{CH:CH} \\ \text{CS-CH} \end{smallmatrix} \text{CH}$, whilst the colourless solutions contain salts of the true mercaptan. The cuprous salt is a reddish-yellow powder. Methyl iodide converts the mercaptan into pyridyl 2-methosulphide, $C_5NH_4 \cdot SMe$, which is a colourless oil boiling at 197° , and possessing a characteristic odour. The hydrochloride forms white crystals, the hydriodide melts at 155 — 157° , the platini-chloride at 185 — 187° , and the picrate at 155° . This sulphide is converted by oxidation into pyridyl-2-methylsulphone, $C_5NH_4 \cdot SO_2Me$, which is a thick oil boiling with partial decomposition at about 325° ; it has only very feebly basic properties, and forms a mercurichloride, $(C_6H_7O_2NS)_2HgCl_2$, which melts at 125° . Pyridyl-2-thioglycollic

acid, $C_5NH_4 \cdot S \cdot CH_2 \cdot CO_2H$, is obtained by the action of chloroacetic acid on the mercaptan, and forms yellowish crystals melting at 127° . The *hydrochloride* also forms yellowish crystals and melts at $166-167^\circ$.

2-Pyridyl sulphide is not formed by the action of potassium sulphide on chloropyridine, pyridylmercaptan being the sole product. 2-Pyridyl disulphide, $C_5NH_4 \cdot S \cdot S \cdot C_5H_4N$, obtained by the action of iodine on the mercaptan, crystallises in needles melting at $57-58^\circ$, and is only a weak monacid base. The *platinichloride* melts at 150° , and the *picrate* at 119° . Pyridine-2-sulphonic acid, $C_5H_4N \cdot SO_3H$, is produced by the action of dilute nitric acid on the mercaptan, and crystallises in needles melting at $239-240^\circ$. The *barium* salt is readily soluble, and the *silver* salt sparingly so in water.

2:6-Lutidyl 4-mercaptan, $C_5NH_3Me_2 \cdot SH$, forms yellow crystals melting at 224° , and yields colourless solutions in both acids and alkalis, which probably contain salts of the tautomeric thiolutidone, $C_5NH_3Me_2 \cdot S$. The compounds with acids are stable; the *hydrochloride* forms white crystals which melt at 258° , and the *picrate* melts at 179° . 2:6-Lutidyl 4-methosulphide, $C_7H_8N \cdot SMe$, melts at 51° , boils at 233° , and crystallises from water with $3H_2O$. The *hydriodide* melts at $224-225^\circ$, the *dichromate* melts and decomposes at 160° , and the *platinichloride* at 245° , whilst the *picrate* melts at 169° .

2:6-Lutidyl-4-methylsulphone crystallises in long, white, silky needles, and is a well-marked base. The *platinichloride* melts and decomposes at 226° , the *dichromate* at 119° , and the *picrate* at 221° .

Lutidyl acetonyl sulphide, $C_7NH_8 \cdot S \cdot CH_2 \cdot COMe$, is obtained by the action of chloroacetone on the mercaptan, and crystallises in lustrous white needles melting at $83-84^\circ$. The *hydrochloride* melts and decomposes at 225° , the *platinichloride* melts at $126-127^\circ$, and the *picrate* at $181-182^\circ$. The *oxime* forms white crystals melting at $122-123^\circ$.

2:6-Lutidyl 4-sulphide, $(C_7H_8N)_2S$, is readily formed by the action of potassium sulphide on chlorolutidine and melts at $82-83^\circ$; it is a diacid base, the *platinichloride* melting at 268° , and the *picrate* at $206-207^\circ$, whilst the *dichromate* decomposes explosively at 180° . Di-2:6-lutidyl-4-sulphone, $SO_2(C_7H_8N)_2$, forms long, white needles melting at 114° , and is a diacid base. The *nitrate* can be recrystallised from alcohol, and decomposes at 175° ; the *platinichloride* melts and decomposes at 262° , the *dichromate* at 185° , and the *picrate* also at 185° . The *monopicrate* melts at $193-194^\circ$. 2:6-Lutidyl 4-disulphide, $C_7H_8N \cdot S \cdot S \cdot C_7H_8N$, forms white crystals melting at 57° , and is a diacid base. The *platinichloride*, *picrate*, and *dichromate* decompose when heated without melting. The disulphide is also produced by the oxidation of the mercaptan with nitric acid, potassium permanganate, and, quantitatively, with hydrogen peroxide in neutral solution; it is very readily reduced to the mercaptan. Hydrogen peroxide, on the other hand, in alkaline solution, converts the mercaptan into 2:6-lutidyl-4-sulphonic acid, $C_7H_8N \cdot SO_3H$, which forms white crystals, and is unaffected by being heated to 300° . The *barium* salt is readily soluble, and the *silver* salt sparingly so in water.

A. H.

Action of Hypochlorous Acid on Tertiary Amines. By RICHARD WILLSTÄTTER and FRITZ IGLAUER (*Ber.*, 1900, 33, 1636—1641).—Hypochlorous acid interacts vigorously with tertiary amines to form a dialkyl nitrogen chloride (iminochloride) by the elimination of an alkyl radicle, thus: $\text{NR}^1\text{R}^{11}\text{R}^{111} + \text{HClO} = \text{NR}^1\text{R}^{11}\text{Cl} + \text{R}^{111}\text{OH}$; it is possible that the additive compound, $\text{NR}^1\text{R}^{11}\text{R}^{111}\text{Cl}(\text{OH})$, is initially formed in this action, although, in view of the stability of compounds of the latter type (the hydrochlorides of the dialkylamine oxides, compare especially Bamberger and Tschirner, *Abstr.*, 1899, i, 347) this appears hardly probable.

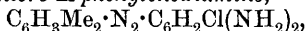
$\text{CH}_2 \cdot \overset{\text{CH}}{\underset{\text{CH}_2}{\text{CH}}} \cdot \overset{\text{CH}}{\underset{\text{CH}_2}{\text{CH}}}$

Chloronortropidine, $\left| \begin{array}{c} \text{NCl} \text{CH} \\ \text{CH}_2 \cdot \text{CH} \cdot \text{CH}_2 \end{array} \right|$, is formed on adding tropidine to an aqueous solution of hypochlorous acid (compare Einhorn, *Abstr.*, 1890, 90); the yield is good. It boils at $79-80^\circ$ under 15 mm. pressure, has a pungent, irritating odour, is volatile with steam, and slowly decomposes on keeping. It has the properties of a weak base, since it dissolves in dilute mineral acids, and is recovered unchanged on adding ammonium sulphate; it is easily reduced by zinc dust and water or aqueous sodium hydrogen sulphite to *nortropidine*, $\text{CH}_2 \cdot \overset{\text{CH}}{\underset{\text{CH}_2}{\text{CH}}} \cdot \overset{\text{CH}}{\underset{\text{CH}_2}{\text{CH}}}$ $\left| \begin{array}{c} \text{NH} \text{CH} \\ \text{CH}_2 \cdot \text{CH} \cdot \text{CH}_2 \end{array} \right|$, which boils at 160° (corr.), is miscible with hot water, and yields a crystalline *carbonate*, a well defined *nitrosoamine*, a sparingly soluble *picrate*, and a beautifully crystalline *platinichloride*.

Hypochlorous acid converts tropane into an iminochloride which on reduction yields nortropan (norhydrotropidine), whilst with N-methylpiperidine, piperylene nitrogen chloride (Bally, *Abstr.*, 1888, 964; Lellman and Geller, *ibid.*, 970) is obtained. W. A. D.

4-Chloro-*m*-phenylenediamine. By PAUL COHN and ARMIN FISCHER (*Monatsh.*, 1900, 21, 267—279).—4-Chloro-*m*-phenylenediamine, prepared by reduction of 4-chloro-*m*-dinitrobenzene, crystallises in the rhombic system [$a : b : c = 1 : 0.7106 : 0.6375$], is easily soluble in alcohol, chloroform, or hot water, and melts at 91° , not 86° as stated by Beilstein and Kurbatoff (*Abstr.*, 1879, 144). The aqueous solution reduces silver nitrate solution and is rapidly oxidised by ferric chloride or potassium dichromate, a property which characterises the salts which for the most part are crystalline, colourless, soluble in water, and insoluble in organic solvents. The following were prepared: the *hydrochloride*, which decomposes at 205° , the *platinichloride*, *sulphate*, *oxalate*, and *tartrate*. The *acetyl* derivative melts at 170° and the *dibenzoyl* derivative at 178° .

as-m-Xyleneazo-4-chloro-m-phenylenediamine,



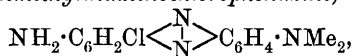
prepared by treating the chlorophenylenediamine with diazotised *as-m*-xylylidine crystallises in fine, reddish-yellow needles, easily soluble in organic solvents and sparingly in water, and melts at 150° .

p-Tolueneazo-4-chloro-m-phenylenediamine, $\text{C}_6\text{H}_4\text{Me} \cdot \text{N}_2 \cdot \text{C}_6\text{H}_4\text{Cl}(\text{NH}_2)_2$, prepared in an analogous manner, crystallises in fine, orange-red

leaflets, is soluble in hot water and organic solvents, and melts at 172°.

Benzeneazo-4-chloro-m-phenylenediamine, $N_2Ph \cdot C_6H_2Cl(NH_2)_2$, made by the action of diazobenzene chloride, forms lustrous, orange-red leaflets, is soluble in organic solvents and hot water, and melts at 151°.

The eurhodine, *dimethylhydiuminoklorophenazine*,



prepared by the action of *p*-nitrosodimethylaniline, is easily soluble in alcohol and water, and gives with acids the colour reactions characteristic of this class of compounds.

1:2:4-Trichlorobenzene was prepared by Sandmeyer's reaction. 1-Nitro-2:4:5-trichlorobenzene melts at 55°, not 57°, as stated.

R. L. J.

Condensation of Ethyl Cetipate with *o*-Diamines. I. Condensation with Ethylenediamine and the Naphthylene-*o*-diamines. By RENE THOMAS-MAMERT and ST. WEIL (*Bull. Soc. Chim.*, 1900, [iii], 23, 438—456).—The condensation products of ethyl cetipate (oxaldiacetate) with diamines are characterised by the facility with which the adjacent $CH_2 \cdot CO_2Et$ groups interact to form a pentatomic closed chain. The nucleus, $C_6H_4 \begin{array}{c} \text{N} : \text{C} : CH_2 \\ \diagup \quad \diagdown \\ \text{N} : \text{C} : CH_2 \end{array} > CO$, which is contained in many of the compounds described, is designated phenoketopentamethyleneazine.

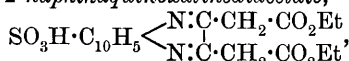
Ethyl dihydropyrazine-2:3-diacetate, $C_4N_2H_4(CH_2 \cdot CO_2Et)_2$, obtained by gently warming ethylenediamine with an alcoholic solution of ethyl cetipate, crystallises in large, yellow needles melting at 100°, and is hydrolysed by concentrated hydrochloric acid to the *hydrochloride*, $\begin{array}{c} CH_2 \cdot N = \\ CH_2 \cdot N(HCl) : \end{array} \begin{array}{c} C : CH_2 \\ C : CH(CO_2H) \end{array} > CO$, which crystallises in microscopic, green needles.

Ethyl 1:2-naphthaquinooxalinediacetate, $C_{10}H_6 \begin{array}{c} \text{N} : \text{C} : CH_2 \cdot CO_2Et \\ \diagup \quad \diagdown \\ \text{N} : \text{C} : CH_2 \cdot CO_2Et \end{array}$, from ethyl cetipate and 1:2-naphthylenediamine, crystallises in highly refractive, brownish-yellow needles melting at 98°, and is converted by the action of alcoholic potash into the corresponding *potassium salt*, which crystallises well. This, when heated with dilute sulphuric acid, yields (1) the dibasic acid, $C_{10}H_6 \begin{array}{c} \text{N} : \text{C} : CH_2 \cdot CO_2H \\ \diagup \quad \diagdown \\ \text{N} : \text{C} : CH_2 \cdot CO_2H \end{array}$, which, however, was not isolated; (2) 1:2-naphtha- β -ketopentamethylenazinecarboxylic acid, $C_{10}H_6 \begin{array}{c} \text{N} : \text{C} : CH_2 \\ \diagup \quad \diagdown \\ \text{N} : \text{C} : CH(CO_2H) \end{array} > CO$, which crystallises in slender, yellow needles decomposing, without melting, at 190°; (3) naphtha-ketopentamethylenazine, which was separated by means of its *bromine derivative*, $C_{10}H_6 \begin{array}{c} \text{N} : \text{C} : CHBr \\ \diagup \quad \diagdown \\ \text{N} : \text{C} : CH_2 \end{array} > CO$, crystallising in yellow needles which remain unmelted at 275°, and its *sulphate*, $C_{15}H_{10}ON_2 \cdot H_2SO_4$, which crystallises in brown needles and decomposes, without melting, above 262°.

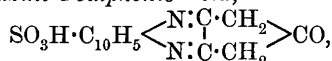
Ethyl 1:2-naphtha-β-ketopentamethylenazinecarboxylate, obtained by the action of sodium ethoxide on ethyl 1:2-naphthaquinoxalinediacetate, crystallises in large, golden-yellow, silky needles which decompose, without melting, at about 250°; its solution in chloroform has a magnificent green fluorescence, whilst its solution in concentrated sulphuric acid is of a blood-red colour. The corresponding acid crystallises in yellow needles which decompose at 190°, and is shown by its great stability to have most probably the enolic formula,

$$\text{C}_{10}\text{H}_6 \begin{array}{c} \text{N}:\text{C}=\text{CH} \\ | \\ \text{N}:\text{C}\cdot\text{CH}(\text{CO}_2\text{H}) \end{array} \text{C}\cdot\text{OH}.$$

Ethyl 4-sulpho-1:2-naphthaquinoxalinediacetate,



obtained by treating ethyl cetipate with 1:2-naphthylenediamine-4-sulphonic acid in acetic acid solution, crystallises in greenish-yellow, microscopic needles which remain unaltered at 285°. The corresponding acid crystallises in brown needles, which are unaltered by heating at 275°, and is converted by boiling with water into 1:2-naphtha-β-ketopentamethylenazine-4-sulphonic acid,



which crystallises with 1H₂O and is unaltered by heating at 230°.

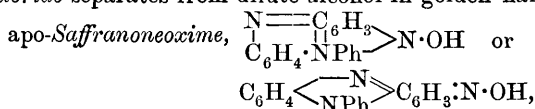
Ethyl 2:3-naphthaquinoxalinediacetate, formed by the action of 2:3-naphthylenediamine on ethyl cetipate, crystallises in orange, cauliflower-like masses melting at 139.5°. The analysis of this compound presented considerable difficulties on account of the slowness with which it undergoes combustion. In this respect, it was found to resemble *o*-diphenyl-2:3-naphthaquinoxaline, obtained in an analogous manner from benzil and 2:3-naphthylenediamine, which forms microscopic, yellow crystals melting at 189.5–190°. When treated successively with sodium ethoxide and sulphuric acid, ethyl 2:3-naphthaquinoxalinediacetate yields the sulphate of ethyl 2:3-naphtha-β-ketopentamethylenazinecarboxylate, $\text{C}_{10}\text{H}_6 \begin{array}{c} \text{N}:\text{C}\cdot\text{CH}(\text{CO}_2\text{Et}) \\ | \\ \text{N}:\text{C}\text{---}\text{CH}_2 \end{array} \text{CO}$, a dark yellow powder which decomposes, without melting, at about 200°.

N. L.

Saffranine and Rosinduline. By OTTO FISCHER and EDUARD HEPP [with FRIED. LINNEMANN, ALEXANDER GUTBIER, and WALTHER DILTHEY] (*Ber.*, 1900, 33, 1485–1498. Compare *Abstr.*, 1898, i, 334). —*apo-Saffranine hydrobromide*, $\text{C}_{18}\text{H}_{14}\text{N}_3\text{Br}$, crystallises from alcohol in dark red prisms with a green lustre. *apo-Saffranone chlorobromide* (chlorophenylphenazonium bromide), $\text{C}_6\text{H}_5\text{Cl} \begin{array}{c} \text{N} \\ \text{NPhBr} \end{array} \text{C}_6\text{H}_4$, crystallises from methyl alcohol in brownish-red, glistening flakes. *apo-Saffranone platinichloride*, $(\text{C}_{18}\text{H}_{12}\text{N}_2\text{Cl})_2\cdot\text{PtCl}_6$, separates from dilute alcohol in dark reddish-brown needles with a blue lustre; the *aurichloride*, $\text{C}_{18}\text{H}_{12}\text{N}_2\text{ClAuCl}_4 + \text{H}_2\text{O}$, forms long needles with a blue lustre.

p-Tolylaposafranine bromide, $\text{C}_7\text{H}_7\cdot\text{NH}\cdot\text{C}_6\text{H}_3 \begin{array}{c} \text{N} \\ \text{NPhBr} \end{array} \text{C}_6\text{H}_4$, prepared by the action of *p*-toluidine on *aposafranine* bromide, separates

from dilute alcohol in bronze-like needles; the *base* crystallises from a mixture of alcohol and benzene, and melts at 196° ; the *platini-chloride* separates from dilute alcohol in golden flakes.



prepared by the action of hydroxylamine hydrochloride on *apo-saffranone* in presence of concentrated potassium hydroxide solution, is insoluble in water, crystallises from dilute alcohol, has a very high melting point, forms salts with strong acids, and resembles *apo-saffranone* in giving a dichroic solution in sulphuric acid. The basic *aurichloride*, $(\text{C}_{18}\text{H}_{13}\text{N}_3\text{O})_2 \cdot \text{HAuCl}_4$, forms dark green, glistening crystals.

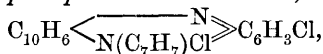
iso-Rosindoneoxime, $\begin{array}{c} \text{N}=\text{C}_6\text{H}_3 \\ | \\ \text{C}_{10}\text{H}_6 \cdot \text{NPh} \end{array} \text{---} \text{N} \cdot \text{OH}$, prepared in a similar way from *isorosindone*, crystallises from dilute alcohol in greenish, lustrous prisms; the *hydrochloride* crystallises in bluish needles.

7-Ethylisorosindoneoxime, $\begin{array}{c} \text{N}=\text{C}_6\text{H}_3 \\ | \\ \text{C}_{10}\text{H}_6 \cdot \text{NEt} \end{array} \text{---} \text{N} \cdot \text{OH}$, resembles the preceding compound; the *hydrochloride* crystallises in bluish, lustrous needles.

7-o-Tolylisorosindone, $\begin{array}{c} \text{N}=\text{C}_6\text{H}_3 \\ | \\ \text{C}_{10}\text{H}_6 \cdot \text{N}(\text{C}_7\text{H}_7) \end{array} \text{---} \text{O}$, prepared by condensing *p*-nitrophenol with *o*-tolyl- β -naphthylamine, crystallises from alcohol in dark red needles, melts at 148° , and closely resembles *rosindone*. The *hydrochloride* crystallises from dilute hydrochloric acid in orange-red flakes. The less soluble *hydrobromide* forms green, glistening crystals. The *aurichloride* forms dark red, glistening needles.

7-o-Tolylrosindoneoxime, $\begin{array}{c} \text{N}=\text{C}_6\text{H}_3 \\ | \\ \text{C}_{10}\text{H}_6 \cdot \text{N}(\text{C}_7\text{H}_7) \end{array} \text{---} \text{N} \cdot \text{OH}$, forms a resinous mass with a green shimmer. The *hydrochloride* crystallises from a mixture of alcohol and ether in glistening prisms. The basic *aurichloride*, $(\text{C}_{23}\text{H}_{17}\text{N}_3\text{O})_2 \cdot \text{HAuCl}_4$, crystallises from water in well-formed, green, glistening needles.

7-Chloro-7-o-tolyl-naphthaphenazonium chloride,

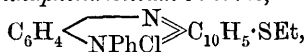


prepared by the action of phosphorus pentachloride on the indone, separates from a mixture of alcohol and ether in stout, yellowish-brown crystals with a blue shimmer. The *hydrochloride* is readily soluble in alcohol and in water, and reacts with bases in the same way as *isorosindone chloride*. The *platinichloride*, $(\text{C}_{23}\text{H}_{16}\text{N}_2\text{Cl})_2 \cdot \text{PtCl}_6$, forms long, orange-yellow tablets. The *aurichloride*, $\text{C}_{23}\text{H}_{16}\text{N}_2\text{ClAuCl}_4$, crystallises from dilute alcohol or from water in yellowish-brown, golden-glistening flakes.

Thiorosindone, $\begin{array}{c} \text{N}=\text{C}_{10}\text{H}_5 \\ | \\ \text{C}_6\text{H}_4 \cdot \text{NPh} \end{array} \text{---} \text{S}$, prepared by the action of potassium hydrosulphide on the chloride, crystallises from pyridine in dark blue

flakes with a metallic lustre, is insoluble in water, and only slightly soluble in organic solvents; it is hydrolysed only slowly by heating with concentrated hydrochloric acid under pressure.

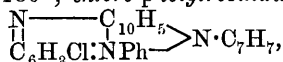
Ethylthiophenyl-naphthaphenazonium chloride,



prepared by the action of mercury mercaptide on rosindone chloride, crystallises from alcohol in glistening, brown needles.

iso-Rosindine chloride, $\text{C}_{10}\text{H}_6 \begin{array}{c} \text{N} \\ \text{---} \\ \text{NPhCl} \end{array} \text{C}_6\text{H}_3\text{Cl}$, crystallises from absolute alcohol in yellowish-red, green-glistening needles. The *ferrichloride* crystallises from alcohol in yellow needles, the *mercurichloride* forms yellowish-red needles, and the *thiocyanate* crystallises in brown needles. Unlike rosindone chloride, *isorosindone* chloride is not readily hydrolysed; on heating with water, it is converted into *isorosindone* together with a small amount of *chloro-rosindone*, $\text{C}_6\text{H}_3\text{Cl} \begin{array}{c} \text{N} \\ \text{---} \\ \text{NPh} \end{array} \text{C}_{10}\text{H}_5 \cdot \text{O}$; this is formed in larger quantities on heating *isorosindone* chloride with alkalis, sodium acetate, or sodium phosphate, crystallises from benzene in glistening needles, and melts at 268° .

Whilst *isorosindone* chloride interacts with aniline in alcoholic solution to form phenyl*isorosinduline* chloride, in aqueous solution it gives chiefly chlorophenylrosinduline, identical with that prepared by Kehrman from anilino- β -naphthaquinone and chlorophenyl-*o*-phenylenediamine. Similar products are obtained with *p*-toluidine; *p-tolylisorosinduline nitrate*, $\text{C}_{10}\text{H}_6 \begin{array}{c} \text{N} \\ \text{---} \\ \text{NPh}(\text{NO}_3) \end{array} \text{C}_6\text{H}_3 \cdot \text{NH} \cdot \text{C}_7\text{H}_7$, forms steel-blue, glistening needles, whilst the *base* forms violet, glistening tablets, and melts at 186° ; *chloro-p-tolylrosinduline*,



crystallises from a mixture of alcohol and benzene in black flakes, melts at $215\text{--}216^\circ$, and forms a difficultly soluble, red *sulphate*.

Naphthindone is converted by the action of phosphorus pentachloride into 7-chloro-7-phenyl-naphthazonium chloride, $\text{C}_{10}\text{H}_5 \begin{array}{c} \text{N} \\ \text{---} \\ \text{NPhCl} \end{array} \text{C}_{10}\text{H}_5\text{Cl}$; this crystallises from a mixture of alcohol and ether in reddish-yellow, green-glistening needles, and gives a crystalline *platinichloride*, *ferrichloride*, and *mercurichloride*.
T. M. L.

Constitution of the Induline of the Aminoazobenzene Fusion. By OTTO FISCHER and EDUARD HEPP (*Ber.*, 1900, 33, 1498—1503).—The blue induline, $\text{C}_{30}\text{H}_{23}\text{N}_5$, of the amidoazobenzene fusion (Fischer and Hepp, *Abstr.*, 1896, i, 50 and 323) is now shown

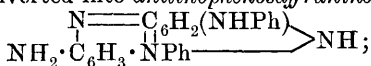
to have the structure $\text{NH}_2 \cdot \text{C}_6\text{H}_3 \cdot \text{NPh} \begin{array}{c} \text{N} \\ \text{---} \\ \text{C}_6\text{H}_2(\text{NPh}) \end{array} \text{NPh}$, and is thus an anilinomauveine or anilinophenylphenosaffranine. The *hydrochloride*, $\text{C}_{30}\text{H}_{24}\text{N}_5\text{Cl} \cdot \frac{1}{2}\text{H}_2\text{O}$, crystallises from alcohol in small, green,

glistening needles; the *hydrobromide*, bronze-like, lustrous needles; the *hydriodide*, green, glistening needles; the *sulphate*, glistening, prismatic crystals and the *picrate*, bronze-like flakes.

With nitrous acid, the induline gives a *diazo*-compound, which, when boiled with alcohol, gives an anilinophenyl*aposafranine*, $\text{N}=\text{C}_6\text{H}_2(\text{NHPh}) \cdot \text{C}_6\text{H}_4 \cdot \text{NPh} \longrightarrow \text{NPh}$, which is identical with that obtained by the action of aniline and aniline hydrochloride on *aposafranine*, and can be hydrolysed to anilino*aposafranone* and aniline, and further to hydroxy*aposafranone* and aniline.

The induline is hydrolysed by dilute sulphuric acid at 230—250° to dihydroxy*aposafranone*, $\text{OH} \cdot \text{C}_6\text{H}_3 \cdot \text{NPh} \xrightarrow{\text{N}=\text{C}_6\text{H}_2(\text{OH})} \text{O}$.

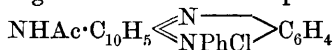
By heating with ammonia and ammonium chloride at 130—140°, the induline is converted into *anilinophenosaffranine*,



the base crystallises from pyridine in green prisms and melts and decomposes at 158°; it forms a soluble *acid sulphate* and a *neutral sulphate*, $(\text{C}_{24}\text{H}_{19}\text{N}_5)_2 \cdot \text{H}_2\text{SO}_4$, which crystallises from dilute alcohol in glistening prisms; the *hydrochloride*, $\text{C}_{24}\text{H}_{19}\text{N}_5 \cdot \text{HCl}$, forms violet needles with a metallic lustre. By the action of nitrous acid and alcohol, the amino-group is removed and the base is converted into anilino*aposafranine*, identical with that prepared from *aposafranine* and aniline, and by the oxidation of *o*-aminodiphenylamine; the formation of this compound proves that the $-\text{NPh}-$ group of the induline is in the ortho-position relatively to the $-\text{NHPh}$ group. The anilino*aposafranine* is converted by zinc dust and acetic acid into *aposafranine* and aniline.

T. M. L.

The Tenth and Eleventh Isomerides of Rosinduline. By FRIEDRICH KEHRMANN and H. WOLFF (*Ber.*, 1900, 33, 1543—1548. Compare *Abstr.*, 1898, i, 154, 155; 1899, i, 238, 525; this vol., i, 60). —7-Acetylamino-1:2-naphthaquinone (compare this vol., i, 449) readily condenses with an alcoholic solution of phenyl-*o*-phenylenediamine hydrochloride, yielding the two isomeric compounds,



(Ph in positions 7 and 12 respectively), which, when hydrolysed, yield the tenth and eleventh *isorosindulines*. The original condensation products are best isolated as their bromides by the addition of solid sodium bromide, and separated by the aid of a moderate quantity of hot water, in which the acetylamino-7-phenylnaphthaphenazonium bromide is almost insoluble.

2-Acetylamino-12-phenylisonaphthaphenazonium 12-bromide, which is formed in much the larger quantity, crystallises from alcohol in chocolate-coloured, glistening plates, and is readily soluble in hot water to a yellowish-brown solution, which does not exhibit fluorescence; its alcoholic solution is coloured violet-blue on the addition of dimethylamine. The *dichromate*, $(\text{C}_{24}\text{H}_{18}\text{ON}_3)_2\text{Cr}_2\text{O}_7$, forms black-brown crystals insoluble in water.

2-Amino-12-phenylisonaphthaphenazonium 12-bromide (isorosinduline No. 10) crystallises in long, black-green prisms, or in small, dark green nodular masses; it dissolves readily in water or alcohol, and its solutions exhibit no fluorescence. The *dichromate*, $(C_{22}H_{16}N_3)_2Cr_2O_7$, forms a dark green, crystalline precipitate insoluble in water.

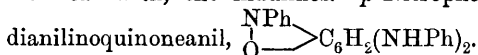
2-Acetamino-7-phenylnaphthaphenazonium 7-bromide crystallises from boiling alcohol in dark brown plates with a bronzy lustre; its solutions have a cherry-red colour, but exhibit no fluorescence.

2-Amino-7-phenylnaphthaphenazonium bromide (isorosinduline No. 11) crystallises in black, glistening prisms, readily soluble in water to bluish-green solutions, and the *dichromate* forms a dark green, crystalline powder.

The constitutions of the two bromides were established by removing the amino-group; the isorosinduline No. 10 gave a phenyliso-naphthaphenazonium salt, and the isomeric compound phenylnaphthaphenazonium.

J. J. S.

Electrolytic Preparation of Colouring Matters Resembling Indulines. By WALTHER LÖB (*Zeit. Elektrochem.*, 1900, 6, 441).—A solution of 2 parts of aniline in 1 part of aqueous hydrochloric acid (sp. gr. 1.19) readily dissolves aromatic nitro-compounds. Such solutions, when reduced at the cathode of an electrolytic cell, yield colouring matters which resemble, though they are probably not identical with, the indulines. *p*-Nitrophenol gives a good yield of



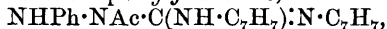
T. E.

Phenylhydrazone-carbo- and -dicarbo-diimine. The Decomposition Product of Wessel's Dicarbo-base. By CARL SCHALL (*J. pr. Chem.*, 1900, ii, 61, 440—448. Compare Abstr., 1893, i, 461; and Wessel, Abstr., 1888, 1083).—Wessel's base gives a dark yellow *dinitroso*-derivative, $C_{32}H_{26}N_6(NO)_2$, which melts and decomposes at 112°. The decomposition product, $C_{20}H_{16}ON_3$ (Abstr., 1893, i, 461), has been prepared by the action of carbonyl chloride on anilino-diphenylguanidine, and is therefore regarded as having the formula

$$\begin{array}{c} \text{NPh} \text{---} \text{N} \\ | \\ \text{CO} \cdot \text{NPh} \end{array} \text{---} \text{C} \cdot \text{NHPh}.$$

Phenylhydrazoncarbodi-*p*-tolylamine melts at 168—170° and not at 138° (Wessel, *loc. cit.*); it is readily oxidised by mercuric oxide to the *azo*-derivative, $\text{NPh} \cdot \text{N} \cdot \text{C}(\text{NH} \cdot \text{C}_7\text{H}_7) \cdot \text{NC}_7\text{H}_7$, which forms deep-red needles and melts at 115°.

Acetylphenylhydrazonedi-p-tolylguanidine,



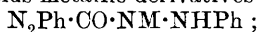
prepared from acetylphenylhydrazine and carbodi-*p*-tolylimide, crystallises from alcohol in white needles and melts at 200°. The *dibromo*-derivative, $C_{23}H_{22}ON_4Br_2$, melts at 215°; the *nitro*-derivative, $C_{21}H_{21}N_4 \cdot NO_2$, which does not contain an acetyl group, is a dark-red compound, and melts at 208°.

T. M. L.

Electrolytic Reduction of *p*-Nitroaniline. By H. SONNEBORN (*Zeit. Elektrochem.*, 1900, 6, 509).—The electrolytic reduction of *p*-nitroacetanilide in neutral solution, by the method of Elbs (*Zeit. Elek-*

trochem., 1898, 5, 9), with a current density of 0.014 ampere per sq. cm. at the cathode, gave a yield of 30 to 40 per cent. of the theoretical quantity of diacetyl-*p*-diaminoazoxybenzene, and 50 to 60 per cent. of the theoretical quantity of acetyl-*p*-phenylenediamine. It was not found possible to reduce the diacetylazoxy-compound itself further, but *p*-diaminoazoxybenzene was readily reduced electrolytically to the corresponding azo- and hydrazo-compounds. When the solution of *p*-nitroacetanilide is slightly acidified with acetic acid, the reduction yields acetyl-*p*-phenylenediamine, and none of the azoxy-compound. T. E.

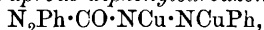
Metallic Compounds of Diphenylcarbazone. By PAUL CAZENEUVE (*Compt. rend.*, 1900, 130, 1478—1479).—Diphenylcarbazone, $N_2Ph \cdot CO \cdot NH \cdot NHPh$, obtained by the action of oxidising agents on *s*-diphenylcarbazide, yields metallic derivatives of the type



the *potassium* and *sodium* derivatives are produced either by heating the diphenylcarbazide with alcoholic potash or soda, or by treating it with potassium or sodium in toluene solutions. These alkali derivatives yield the *zinc*, *lead*, *copper*, *mercury*, *iron*, *chromium*, *cobalt*, and *nickel* compounds by double decomposition with the metallic acetates. These substances are soluble in alcohol, benzene, carbon disulphide, or chloroform, but not in water. Platinic chloride gives a *platinum* derivative, but gold chloride and silver salts are reduced by the alkali derivatives of diphenylcarbazone.

These metallic derivatives are all decomposed by heat at temperatures below 100°. G. T. M.

Cuprous and Mercurous Derivatives of Diphenylcarbazone. By PAUL CAZENEUVE (*Compt. rend.*, 1900, 130, 1561—1563. Compare preceding abstract).—*Cuprous diphenylcarbazone*,



prepared by adding an alcoholic solution of *s*-diphenylcarbazide (1 mol.) to an aqueous solution of copper acetate (2 mols.), forms a deep violet precipitate which decomposes explosively at temperatures below 100°; it is soluble in the ordinary organic solvents. The cuprous compound slowly decomposes when exposed to moist air, and when dissolved in chloroform containing a little alcohol it is rapidly destroyed, yielding *carbodiazone*, $CO(N:NPh)_2$, and cuprous chloride.

The production of the cuprous derivative from diphenylcarbazide affords a means of detecting minute traces of copper, the reaction being even more sensitive than that obtained with ferrocyanide; since the product is decomposed by mineral acids, it is, however, necessary to operate in neutral solutions.

Mercurous diphenylcarbazone, obtained from aqueous solutions of mercuric acetate as a deep blue precipitate, resembles its cuprous analogue, but is far more stable, and may also be prepared by heating diphenylcarbazide and mercury at 170—200°.

The production of this compound constitutes a delicate test for mercury in combination with nitric and the organic acids; the mercuric haloids and cyanide, however, do not give this reaction.

G. T. M.

Preparation of a Pure Albumin from White of Egg. By F. GOWLAND HOPKINS (*J. Physiol.*, 1900, 25, 306—330).—In crystallised egg-albumin there are undoubtedly several proteids; this is shown by the varying rotation and percentage of sulphur in different fractions. Much the same is true for serum-albumin, but the principal experiments here recorded relate to egg-albumin. A modification of the methods previously described led to the preparation of one of these egg-albumins in a crystalline form, which, after repeated fractional crystallisation, shows absolute constancy of rotation (-30.7°) and a constant proportion of sulphur (1.57 per cent.); it is practically ash free. The yield is 50 grams and upwards per litre of egg-white. The crystals obtained by the use of ammonium sulphate may be washed free from that salt by a saturated solution of sodium chloride containing 1 per cent. of acetic acid; the crystals retain their form and solubility in water, and ammonium sulphate does not enter into their composition. Comparatively little importance is attached to the kind of acid used in the preparation of the crystals. W. D. H.

Formation of Bases from Albumin. By RUDOLF COHN (*Zeit. Physiol. Chem.*, 1900, 29, 283—302).—The compound melting at 295° (Abstr., 1896, 1, 658), obtained by the action of hydrochloric acid on casein, is not, as previously stated, a pyridine derivative, and, on the other hand, is not identical, as was thought at one time, with leucinimide obtained from leucine (from casein), as the latter melts 33° lower. Although the analyses do not agree very well, and the carbon is 0.9 per cent. too high, the author thinks the compound may be isomeric with leucinimide.

Leucinimide, when reduced with sodium and alcohol, yields a base distilling at $220-270^\circ$; the *hydrochloride*, $C_{12}H_{26}N_2 \cdot 2HCl$, can be crystallised from concentrated hydrochloric acid; the *nitrate* crystallises in small plates, and is only sparingly soluble in cold water; and the *platinichloride* crystallises in pale yellow plates. The constitution $NH \begin{smallmatrix} \diagup CH(C_4H_9) \cdot CH_2 \\ \diagdown CH_2 \cdot CH(C_4H_9) \end{smallmatrix} NH$ is suggested for the base, and $NH \begin{smallmatrix} \diagup CH(C_4H_9) \cdot CO \\ \diagdown CO \cdot CH(C_4H_9) \end{smallmatrix} NH$ for leucinimide. The compound melting at 295° appears to yield the same base when reduced. J. J. S.

Nucleic Acid from Various Sources. By LÉON HERLANT (*Chem. Centr.*, 1900, i, 870; from *Arch. exp. Path. Pharm.*, 44, 148—159).—Nucleic acid from unripe salmon sperm was isolated by the "copper-potash method," and the formula of the acid is given as $C_{40}H_{56}N_{14}O_{16}(P_2O_5)_2$. That from calf's thymus has the same formula. That from yeast yields, on decomposition, guanine, adenine, and a reducing substance. W. D. H.

Proteids. By ALBRECHT KOSSEL and FR. KUTSCHER (*Sitzungsber. Ges. gesammte. Naturwissensch. Marburg*, 1900, April 6).—Further investigations into the protamines and proteids proper, with special reference to the bases obtainable from them, leads to the following classification. The protamines that contain a monohexon nucleus

(arginine) fall into two groups, those which yield tyrosine, namely, cyclopteryne, and those which do not, namely, salmine, clupeine, and scombrine. No protamine with a dihexon nucleus is known. Sturine is an instance of a protamine which contains a trihexon nucleus, that is, it yields lysine, arginine, and histidine; it is free from tyrosine. Passing to the proteids proper, none with a monohexon nucleus is known; those with a dihexon nucleus are gluten-fibrin, mucedin, gliadin, and spongin; these yield arginine and histidine, except spongin, which yields arginine and lysine. The proteids with a trihexon nucleus are histon (?), casein, fibrin, fibrin-peptone, gluten-casein, gelatin, and elastin.

W. D. H.

Glutineptone Hydrobromide and Hydriodide. By CARL PAAL (*Chem. Zeit.*, 1900, 24, 145. Compare Abstr., 1892, 895; 1898, i, 456; and Levites, *Chem. Zeit.*, 1900, 24, 97).—Quantitative yields of these salts have been obtained by methods similar to that employed in the preparation of the hydrochloride. When concentrated aqueous solutions of the salts are supersaturated with ammonium sulphate, the propeptone salts are precipitated, and may be isolated by extraction with absolute methyl alcohol; the true peptone salts remain in solution and may be separated from the ammonium sulphate by precipitating the latter with absolute ethyl alcohol. The *hydrobromide*, like the hydrochloride, is stable, but the *hydriodide* readily turns yellow, and when kept for some time evolves ethyl iodide and yields the free peptone. Neither salt reacts with Millon's reagent.

J. J. S.

Thymine. By H. STEUDEL and ALBRECHT KOSSEL (*Zeit. physiol. Chem.*, 1900, 29, 303—306).—When thymine is treated with phosphorus oxychloride according to Gabriel and Colman's method (Abstr., 1899, i, 638), a product is obtained which is somewhat similar to, and probably isomeric with, their 2:6-dichloro-4-methylpyrimidine. This *dichlorothymine*, $C_5H_4N_2Cl_2$, crystallises in plates, melts at 25—26°, is readily soluble in most solvents, and has a characteristic odour.

J. J. S.

Amount of Iron Present in the Hæmoglobin of the Horse. By LOUIS LAPICQUE and H. GILARDONI (*Compt. rend.*, 1900, 130, 1333—1335).—Considerable discrepancy exists between the recorded values of the amount of iron present in the hæmoglobin of the horse; Hoppe-Seyler and the earlier investigators gave the percentage as 0.45—0.47, whilst Bunge and also Zinoffski found 0.335. The composition of the hæmoglobin, rapidly extracted from fresh blood by Jacquet's process, is invariable, the analyses of several preparations giving a practically constant amount, namely, 0.29—0.30; the product obtained by the older and slower methods is less uniform, and the percentage of iron varies from 0.29 to 0.34. This variation is probably due either to changes produced by the putrefaction of the blood or to the action of the chemical agents employed by some investigators in removing the stroma.

These results tend to show that in the blood itself there is only one variety of hæmoglobin, and that the differentiation into several modifi-

cations, containing different amounts of iron, takes place during extraction (compare Cazeneuve and Breteau, *Abstr.*, 1899, ii, 440).

G. T. M.

Hydrolysis of Fibrous Tissue. By ALEXANDRE ETARD (*Compt. rend.*, 1900, 130, 1263—1265).—When the dried ligamentum nuchæ of the ox is boiled with 20 per cent. sulphuric acid for 24 hours, the product neutralised with chalk, and the filtrate concentrated, a crystalloid substance is obtained which has the colour, taste, and consistence of candied honey. The yield of this product is 116.5 per cent., calculated on the weight of fibrous tissue taken, and if the latter substance be assumed to have the simplified formula, $C_{48}H_{78}N_{13}O_{16}$, then the hydrolysis takes place in accordance with the following equation: $C_{48}H_{78}N_{13}O_{16} + 10H_2O = 3NH_3 + C_{48}H_{78}N_{10}O_{26}$. Leucine could not be detected in the product of hydrolysis; the latter, on oxidation with chromic acid mixture, yields ammonium sulphate, oxalic and carbonic acids, traces of hydrocyanic acid, but no acids of the acetic series. The substance behaves quite unlike leucine when distilled with lime or zinc dust, the amount of pyridine bases formed being barely 3 per cent.

G. T. M.

Action of Papain on Pepsin and Pancreatin. By V. HARLAY (*J. Pharm.*, 1900, [vi], 11, 466—469).—Not only are pancreatin and papain without destructive action on each other, but the digestive action of either one is favoured by the presence of the other. Pepsin is without action on papain, but papain in a neutral or slightly acid medium partially destroys pepsin.

H. R. LE S.

Tyrosinase. By C. GESSARD (*Compt. rend.*, 1900, 130, 1327—1330).—A decoction of tyrosinase in glycerol, obtained from mushrooms by Bourquelot's method, oxidises tyrosine, developing a red coloration, which subsequently turns black; after some time, an amorphous, black precipitate is formed. If a very small quantity of the diastase is employed, the red coloration persists and the precipitate is not produced. This result indicates that the development of the black coloration and the formation of the precipitate is not due to the tyrosinase, but to some other substance which accompanies it in the glycerol extract. The addition of various metallic salts to solutions of tyrosine containing only traces of tyrosinase promotes the formation of the black precipitate, the action being accelerated by heat. Ammonium phosphate and the salts of magnesium and the alkaline earth metals are especially efficacious in promoting this oxidation. The black substance possesses noteworthy adhesive properties, and is completely precipitated on shaking the solution with some finely-divided, insoluble substance such as talc, starch, calcium carbonate, or magnesium phosphate. When a piece of silk is immersed in the red tyrosine solution, the black precipitate is produced on the fibre, and is not removed by treating the fabric with hot water.

G. T. M.

Organic Chemistry.

Quaternary Paraffins. II. By WLADIMIR B. MARKOWNIKOFF (*Ber.*, 1900, 33, 1905—1908. Compare *Abstr.*, 1899, i, 554).—*ββ-Dimethylpentane (trimethylpropylmethane)*, prepared by the action of a slight excess of zinc propyl or zinc iodopropyl on *tert*-butyl iodide, boils at 78° under 743 mm. pressure, and has a sp. gr. 0.6910 at 0°/0°, and 0.6743 at 20°/0°; it is not acted on by concentrated nitric acid, or by dilute nitric acid of sp. gr. 1.125—1.40 after heating for 9 hours at 100°, although on heating the hydrocarbon with acid of sp. gr. 1.235 for 27 hours at 110—115°, the secondary *nitro*-derivative, $\text{CMe}_3 \cdot \text{CHEt} \cdot \text{NO}_2$, is obtained. This boils at 89—90° under 40 mm. pressure, is decomposed on distilling under atmospheric pressure, and has a sp. gr. 0.9520 at 0°/0°, and 0.9401 at 20°/20°; its structure follows from its yielding ethyl *tert*-butyl ketone (boiling at 125.5—126°, and of sp. gr. 0.8258 at 0°/0°, 0.8106 at 20°/0°; compare Wischnegradsky, *Abstr.*, 1875, 878), when its solution in aqueous sodium hydroxide is added to stannous chloride dissolved in hydrochloric acid. That only one *nitro*-derivative is formed during the nitration of the hydrocarbon is shown by the fact that only one *semicarbazone* (melting at 173—174° on rapidly heating) could be isolated from the foregoing ketonic product. The *amine*, $\text{CMe}_3 \cdot \text{CHEt} \cdot \text{NH}_2$, obtained by reducing the *nitro*-derivative, yields an *aurichloride* crystallising in small needles.

ββ-Dimethylpentane was isolated from a fraction of Caucasian naphtha boiling at 78—80° by freezing out the hexanaphthene by means of liquid air, removing tertiary hydrocarbons by fuming sulphuric acid, and finally purifying the oil by digesting successively with nitric acid of sp. gr. 1.15 at 110—115°, and boiling nitric acid of sp. gr. 1.4; the hydrocarbon thus obtained boiled at 78.5—79° under 757 mm. pressure, and had a sp. gr. 0.7083 at 0°/0°, and 0.6921 at 20°/0°. W. A. D.

Hydrogenation of Ethylene in the Presence of Reduced Metals. By PAUL SABATIER and JEAN B. SENDERENS (*Compt. rend.*, 1900, 130, 1761—1764. Compare *Abstr.*, 1897, i, 305, 545).—When a mixture of ethylene and hydrogen is passed over recently reduced cobalt, there is at first a production of ethane accompanied by a rise of temperature; the reaction is, however, not maintained, and as soon as the cobalt becomes slightly carburised, it ceases altogether. At 100—150°, the reaction becomes permanent, and the issuing gas consists of a mixture of ethane, ethylene, and hydrogen, containing traces of higher hydrocarbons of the acetylene series. A certain amount of carbon combines with the cobalt, and as a result the activity of the metal gradually diminishes. At 300°, a small quantity of liquid hydrocarbons is produced, and the gaseous product contains both methane and ethane together with a considerable amount of uncombined ethylene and hydrogen.

Reduced iron has no action on the mixed gases at the ordinary temperature, and even above 180° the action is very slow and decreases as the metal becomes carburised.

The combination of ethylene and hydrogen is not induced by reduced copper at temperatures below 180° . Between 180° and 300° , ethane is practically the sole product of combination, there being no appreciable secondary reaction and no deposition of carbon.

G. T. M.

Action of Acetylene on Cuprous Chloride dissolved in Potassium Chloride Solution. By R. CHAVASTELON (*Compt. rend.*, 1900, 130, 1634—1636).—The purple compound formed when acetylene is passed through potassium chloride solution containing cuprous chloride is identical with the compound C_2H_2, Cu_2Cl_2, Cu_2O , obtained by the action of water on the compound C_2H_2, Cu_2Cl_2 , and its formation is limited by the presence of hydrochloric acid in quantity which must be greater the lower the temperature. If the solution of potassium chloride, saturated with cuprous chloride, contains not less than 4 c.c. of concentrated hydrochloric acid in 100 c.c., the first product of the action of acetylene is a yellow, crystalline compound, whilst the final product forms colourless crystals. The first can be converted into the second by the prolonged action of acetylene, and, on the other hand, the white compound is converted into the yellow by the action of a current of carbon dioxide which slowly removes part of the acetylene.

C. H. B.

Crystalline Compounds of Acetylene with Cuprous and Potassium Chlorides. By R. CHAVASTELON (*Compt. rend.*, 1900, 130, 1764—1766. Compare preceding abstract).—The colourless crystals which have the composition $C_2H_2(Cu_2Cl_2)_2, KCl$, lose one-half of the combined acetylene and become converted into the yellow compound $C_2H_2[(Cu_2Cl_2)_2, KCl]_2$ by washing with ether or with the original solution of cuprous and potassium chlorides. Both these double salts have very low dissociation pressures at the ordinary temperature, and they can therefore be dried in a current of carbon dioxide without decomposition. They dissolve in dilute hydrochloric acid without dissociation, the yellow compound being the more soluble. When treated with water, both compounds yield the substance C_2H_2, Cu_2Cl_2, Cu_2O , whilst cuprous acetylide results from the action of ammonia.

G. T. M.

Mode of Formation of the Compounds $C_2H_2(Cu_2Cl_2)_2, KCl$ and $C_2H_2[(Cu_2Cl_2)_2, KCl]_2$. By R. CHAVASTELON (*Compt. rend.*, 1900, 131, 48—50. Compare preceding abstracts).—In solutions saturated with the yellow compound, the ratio of combined to total cuprous chloride is 0.25, whilst in solutions saturated with the colourless salt this quotient is 0.20.

G. T. M.

Hydrogenation of Acetylene in Presence of Reduced Iron or Cobalt. By PAUL SABATIER and JEAN B. SENDERENS (*Compt. rend.*, 1900, 130, 1628—1630).—When acetylene mixed with an excess of hydrogen is passed over reduced iron, there is no change at

the ordinary temperature, but above 180° condensation takes place with production of ethane, ethylene, and higher hydrocarbons of the ethylene series boiling between 50° and 250° , together with small quantities of benzene and its homologues.

With reduced cobalt above 180° , the acetylene is almost completely converted into ethane, together with some liquid paraffins, the proportion of the latter increasing with the temperature.

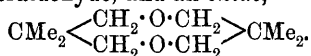
It is clear therefore that different metals produce very different results with mixtures of acetylene and hydrogen. In all cases, if the acetylene is in excess, it is decomposed with liberation of carbon in the manner observed by Moissan and Moureu. C. H. B.

Hydrogenation of Acetylene and Ethylene in the Presence of Finely-divided Platinum. By PAUL SABATIER and JEAN B. SENDERENS (*Compt. rend.*, 1900, 131, 40—42. Compare Abstr., 1899, i, 555).—When a mixture of acetylene and hydrogen containing an excess of the latter is passed over platinum black at the ordinary temperature, the hydrocarbon is completely hydrogenised to ethane; if, however, the acetylene is in excess, both ethylene and ethane are produced. At 180° , the formation of these gaseous products is accompanied by condensations giving rise to liquid hydrocarbons. The catalytic action of platinum black on mixtures of ethylene and hydrogen is only temporary at the ordinary temperature; at 100 — 120° , there is a slow combination, whilst at 185° the reaction is practically quantitative.

Spongy platinum does not induce the hydrogenation of acetylene or ethylene at the ordinary temperature; at 180° , however, it behaves like platinum black. G. T. M.

Action of Reduced Nickel on Acetylene. By PAUL SABATIER and JEAN B. SENDERENS (*Compt. rend.*, 1900, 131, 187—190. Compare Abstr., 1899, i, 553; this vol., i, 197, and preceding abstracts).—A rapid current of acetylene, passed over nickel reduced by hydrogen and cooled in a current of this gas, at once produces incandescence; this reaction is due to the presence of hydrogen, for when it is displaced by nitrogen, there is no appreciable action at temperatures below 180° . At higher temperatures, a slow reaction sets in, and is maintained without incandescence, provided that the current of acetylene is not too rapid; the issuing gas contains hydrogen, ethane, ethylene, together with unchanged acetylene, liquid hydrocarbons containing benzene and the higher olefines are simultaneously produced, and the solid residue appears to consist of a mixture of metallic carbide with a solid hydrocarbon, the latter being analogous to the cuprene obtained from copper and acetylene. When a rapid current of acetylene is employed, the condensation is attended by incandescence, and the issuing gas consists of 51.4 per cent. of hydrogen, 36.3 per cent. of ethane, 2 per cent. of ethylene, 10.3 per cent. of benzene and its homologues, and traces of acetylene; the liquid product is a mixture of aromatic and unsaturated hydrocarbons boiling between 50° and 180° , and the experimental tubes contain a mixture of nickel with carbon and a solid hydrocarbon resembling cuprene. G. T. M.

Action of Sulphuric Acid on Dimethylpropanediol. By ALOIS FISCHER and BERTHOLD WINTER (*Monatsh.*, 1900, 21, 301—318).—Pentaglycol (Abstr., 1894, i, 353), when heated with 20 per cent. sulphuric acid in a sealed tube at 200° for 3 hours, yields methyl isopropyl ketone, isovaleraldehyde, and an oxide,



The last is a colourless, refracting liquid which boils at 180°, yields, when oxidised with alkaline permanganate, dimethylmalonic acid, and, when treated with hydrogen bromide, a mixture of trimethylene dibromide and pentaglycol dibromide.

R. H. P.

A Product of the Decomposition of Glycerol Diiodohydrin. By ERNEST CHARON and C. PAIX SÉAILLES (*Compt. rend.*, 1900, 130, 1631—1633).—The compound of the empirical composition $\text{C}_3\text{H}_5\text{OI}$, formed by the removal of the elements of hydrogen iodide from glycerol diiodohydrin is para- β -iodopropaldehyde; it forms slender, white needles which melt at 160°, sublime very easily, and are very stable when exposed to light, and is best obtained by heating the glycerol diiodohydrin at 100° under reduced pressure, some allyl iodide and polyiodopropanes being also formed. The results obtained by heating the diiodohydrin with alkalis, lead hydroxide, or silver oxide, are less satisfactory. When heated with solid potassium hydroxide, para- β -iodopropaldehyde yields metacraldehyde.

C. H. B.

Partial Synthesis of *l*-Erythritol. By LÉON MAQUENNE (*Bull. Soc. Chim.*, 1900, [iii], 23, 587—591).—The synthesis of *l*-erythritol has been effected by applying to xylose the process of degradation by which Wohl (this vol., i, 140) has obtained *l*-erythrose from *l*-arabinose. A number of new compounds have thus been obtained. *Xylosoxime*, obtained by the action of hydroxylamine on xylose in alcoholic solution, forms an uncrystallisable, viscous mass which becomes semi-fluid at 100°, and is very soluble in water or alcohol. When heated with acetic anhydride and sodium acetate, it is converted into *acetylxylic nitrile*, which crystallises in white or pale yellow scales melting at 81.5°, and is decomposed by alkalis with the production of a considerable quantity of erythrose. By treatment with ammonia (the addition of silver oxide, recommended by Wohl, is considered rather to retard the reaction), the nitrile is converted into *erythrose-acetamide*, which crystallises in small, colourless prisms melting at 166°, and is hydrolysed by mineral acids with the formation of *l*-erythrose, whence *l*-erythritol is obtained by reduction with sodium amalgam. *l*-Erythritol, which was separated by means of its benzaldehyde derivative, crystallises from alcohol in slender needles, and from water in elongated prisms melting sharply at 88°; it is very soluble in water, and is more soluble in hot alcohol than its inactive isomeride. Its rotatory power in 6 per cent. aqueous solution is $[\alpha]_D + 4.3^\circ$, whilst in 1.5 per cent. alcoholic solution it is $[\alpha]_D - 15^\circ$.

N. L.

Methyl Ester and Amide of *d*-Valeric Acid (Methyl-2-butan-*oic* acid) and the Solubility of its Silver Salt. By H. J. TAVERNE (*Rec. Trav. Chim.*, 1900, 19, 107—110).—*Methyl d-valerate*

obtained by saturating a mixture of its generators with hydrogen chloride, is a liquid having an agreeable odour; it boils at 115° under 760 mm. pressure, has a sp. gr. 0.8931 at 15° , and has $[\alpha]_D + 16^{\circ}13'$. The *amide*, prepared by treating the ester with ammonia, crystallises from light petroleum in leaflets melting at 111° ; it has $[\alpha]_D + 18^{\circ}19'$. The solubility of silver *d*-valerate in water is 0.680—0.732 part per 100, and not 1.16 as previously stated. G. T. M.

Telfairia Oil. By HERMANN THOMS (*Arch. Pharm.*, 1900, 238, 48—58).—This oil is contained in the seeds of *Telfairia pedata*, Hook, a gourd-like, climbing plant which grows in East Africa. In a sample from Kwais in Usambara, the kernel formed 60 per cent. of the seed, and contained 64.7 per cent. of oil. The oil had the following constants: sp. gr., 0.9180 at 15° ; acid number, 0.34; saponification number, 174.8; ester number, 174.5; acetyl number, 26.9; iodine number, 86.2; freezing point of the oil, 7° ; melting point of the fatty acids, 44° ; freezing point of the same, 41° ; refractometer number, 61—62 at 31° to 63—64 at 25° . The oil is to a slight extent a drying oil, and it gives an unpleasant odour when heated; for these reasons, and on account of its comparatively high freezing point, it can hardly replace olive oil for culinary purposes. In its hydrolysis, glycerol is formed; the lead salts of the fatty acids were separated by extraction with ether into a solid portion, which contained palmitic and stearic acids, but no hydroxy-acid, and a liquid portion. The latter yielded acids which were separated by distillation under diminished pressure into a new acid, telfairic acid, and a fraction of higher boiling point, approximately having the composition $C_{24}H_{40}O_8$. *Telfairic acid*, $C_{18}H_{32}O_2$, is isomeric with linoleic acid, &c.; it boils at 220 — 225° under 13 mm. pressure, and freezes at 5 — 2° ; it forms a *tetrabromide*, $C_{18}H_{32}O_2Br_4$, which melts at 57 — 58° ; like linoleic acid, it yields tetrahydroxystearic (sativic) acid when oxidised with dilute permanganate at 0° , and azelaic (lepargylic) acid when the oxidation is effected at the ordinary temperature. C. F. B.

Anhydrous Acrylic Acid. By EINAR BIILMANN [in part with BJERRUM] (*J. pr. Chem.*, 1900, [ii], 61, 491—494).—Anhydrous acrylic acid can be prepared by the action of reduced copper containing a trace of iron on $\alpha\beta$ -dibromopropionic acid. The pure anhydrous acid melts at 10.1 — 10.2° , and boils at 140.8 — 141° ; by vigorous boiling, the anhydrous acid polymerises to some extent to a white compound, which was not further investigated. T. M. L.

Glyoxylic Acid. By OSCAR DOEBNER (*Annalen*, 1900, 311, 129—131).—Existing methods for preparing glyoxylic acid are unsatisfactory, but the following process is found to be trustworthy. Dichloroacetic acid (65 parts) is neutralised exactly with potassium hydroxide (1:1) and heated with solid potassium acetate (100 parts) in a reflux apparatus during 1 hour; the filtered liquid, which contains potassium diacetoxycetate, is boiled with 10 volumes of water in a reflux apparatus during several hours, yielding potassium glyoxylate and free acetic acid. M. O. F.

Ethyloxalic Anhydride. By LOUIS BOUVEAULT (*Bull. Soc. Chim.*, 1900, [iii], 23, 509—511).—When ethyloxalic chloride (ethyl chloroglyoxylate) is heated with a mol. proportion of sodium acetate and the product of the reaction fractionally distilled under diminished pressure, the mixed acetic ethyloxalic anhydride first formed is decomposed into the two simple anhydrides. *Ethyloxalic anhydride*, $(\text{CO}_2\text{Et}\cdot\text{CO})_2\text{O}$, is a colourless, oily, very hygroscopic liquid which boils at 135° under 100 mm. pressure. The experiments of Rousset (*Abstr.*, 1895, i, 592) and Béhal (this vol., i, 8) on mixed anhydrides are referred to in connection with the method employed for the preparation of this compound. N. L.

Synthesis of Higher Homologues of Ethyl Acetoacetate and Acetylacetone. By LOUIS BOUVEAULT (*Compt. rend.*, 1900, 131, 45—48).—*Ethyl isobutyrylacetate*, $\text{CHMe}_2\cdot\text{CO}\cdot\text{CHAc}\cdot\text{CO}_2\text{Et}$, produced together with its *isomeride*, $\text{CHMe}_2\cdot\text{CO}\cdot\text{O}\cdot\text{CMe}\cdot\text{CH}\cdot\text{CO}_2\text{Et}$, by the action of isobutyric chloride on the sodium derivative of ethyl acetoacetate, is separated from the latter by dissolving in barium hydroxide solution and reprecipitating with acid; it is a colourless liquid boiling at 114° under 15 mm. pressure; the other compound, which is insoluble in alkaline solutions, is a colourless liquid having a characteristic odour and boiling at 117° under 15 mm. pressure. When hydrolysed with hydrochloric acid and water at 140 — 150° , the isobutyrylacetate is decomposed into methylisopropylacetone, ethyl alcohol, and acetic and carbonic acids.

isoButyrylacetone, $\text{CHMe}_2\cdot\text{CO}\cdot\text{CH}_2\cdot\text{Ac}$, is formed when water only is employed in the preceding hydrolysis; it is a colourless liquid which has an agreeable odour and boils at 168° . It yields a volatile copper salt which dissolves in a mixture of chloroform and petroleum and separates in blue crystals which become pink on exposure to the air.

Ethyl isobutyrylacetate, obtained by hydrolysing ethyl isobutyrylacetate with 1 mol. of sodium hydroxide dissolved in water or alcohol, is a colourless liquid having a fruity odour; it boils at 93 — 94° under 16 mm. pressure. This substance is readily decomposed by alkalis, yielding methylisopropylacetone, ethyl alcohol, and carbon dioxide. G. T. M.

$\alpha\beta$ -Dimethylglutolactonic Acid. By EDMOND E. BLAISE (*Compt. rend.*, 1900, 130, 1716—1719. Compare *Abstr.*, 1896, i, 667).—The semicarbazone of β -methylkævulic acid (m. p. 197°) is produced with some difficulty, and when the reaction is prolonged it decomposes into the acid $\text{N}_2(\text{CMe}\cdot\text{CHMe}\cdot\text{CH}_2\cdot\text{CO}_2\text{H})_2$; this substance, when condensed with hydrogen cyanide, yields a liquid which boils at 144 — 158° under 25 mm. pressure, and contains the nitriles of the isomeric lactonic acids having the general formula $\text{CH}_2\langle\begin{smallmatrix} \text{CHMe} \\ \text{CO}-\text{O} \end{smallmatrix}\rangle\text{CMe}\cdot\text{CN}$.

trans- $\alpha\beta$ -Dimethylglutolactonic acid, $\text{CH}_2\langle\begin{smallmatrix} \text{CHMe} \\ \text{CO}-\text{O} \end{smallmatrix}\rangle\text{CMe}\cdot\text{CO}_2\text{H}$, separates from the product obtained by hydrolysing the mixed nitriles with concentrated hydrochloric acid, in crystals melting at 142° ; it readily dissolves in water, but is somewhat insoluble in cold benzene. The lead salt crystallises in white needles and melts at 212 — 214° .

The *cis-isomeride* is separated from the mother liquors in the form of its *lead* salt, this derivative differing from the corresponding *trans*-compound in crystallising with $1\text{H}_2\text{O}$; the hydrated salt melts at $140\text{--}145^\circ$, whilst the anhydrous substance melts at $181\text{--}183^\circ$. The *acid*, obtained from the lead salt by means of hydrogen sulphide, is a colourless liquid boiling at $193\text{--}195^\circ$ under 15 mm. pressure; when heated with quinoline and water at 180° for 6 hours, it is converted into the *trans*-modification.

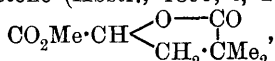
G. T. M.

Oxidation of Cyclic Compounds: α -Methyladipic Acid. By WLADIMIR B. MARKOWNIKOFF (*Ber.*, 1900, 33, 1908—1910).— β -Methylcyclohexanone, on oxidation with nitric acid, gives almost a theoretical yield of what is apparently *α -methyladipic acid*, $\text{CO}_2\text{H}\cdot\text{CHMe}\cdot[\text{CH}_2]_3\cdot\text{CO}_2\text{H}$, melting at $52\text{--}53^\circ$; the *ethyl* salt is laevorotatory, and boils at 160° under 40 mm. pressure, and at $252\text{--}253^\circ$ with partial decomposition under the ordinary pressure. The acid is probably identical with that obtained on oxidising β -methylcyclohexanone with aqueous potassium permanganate, which Wallach first considered to be *α -methyladipic acid* (*Annalen*, 1896, 289, 345), but later (*Ber.*, 1899, 32, 3339) concluded was the β -acid.

The oxidation of pulegone with nitric acid is less simple, a considerable quantity of oxalic acid being formed. β -Methyladipic acid is obtained on oxidising pulegone with aqueous potassium permanganate, as stated by Semmler, and from menthone by a similar process (Manasse and Rupe); but in each case the yield is only 50 per cent. of the theoretical, pyrotartaric acid and other substances being formed.

W. A. D.

Synthesis of $\alpha\alpha$ -Dimethylglutaconic Acid. By MAX CONRAD (*Ber.*, 1900, 33, 1920—1922).—The *methyl* ester of γ -hydroxy- $\alpha\alpha$ -dimethylglutaric acid lactone (Abstr., 1899, i, 259),



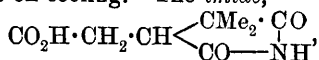
obtained by passing hydrogen chloride into a methyl alcoholic solution of the lactone, crystallises in long, colourless prisms melting at 68° , and when boiled with a solution of sodium in amyl alcohol, then poured into water and again boiled, is converted into $\alpha\alpha$ -dimethylglutaconic acid, $\text{CO}_2\text{H}\cdot\text{CH}\cdot\text{CH}\cdot\text{CMe}_2\cdot\text{CO}_2\text{H}$. This is best purified by conversion into its insoluble barium salt, and after repeated crystallisation melts sharply at 150° . It is probably identical with the acid described by Henrich (Abstr., 1899, i, 469, 794), although he gives the melting point as $126\text{--}133^\circ$.

J. J. S.

Synthesis of Ethyl β -Cyano- $\alpha\alpha$ -dimethyltricarballylate and $\alpha\alpha$ -Dimethyltricarballic Acid. By ALBIN HALLER and G. BLANC (*Compt. rend.*, 1900, 131, 19—22).—Ethyl β -cyano- $\alpha\alpha$ -dimethyltricarballylate, $\text{CO}_2\text{Et}\cdot\text{CH}_2\cdot\text{C}(\text{CN})(\text{CO}_2\text{Et})\cdot\text{CMe}_2\cdot\text{CO}_2\text{Et}$, produced by heating together in absolute alcohol molecular proportions of ethyl cyanosuccinate, sodium ethoxide, and ethyl α -bromoisobutyrate, is a colourless liquid with an alliaceous odour and boils at $205\text{--}206^\circ$ under 21 mm. pressure.

$\alpha\alpha$ -Dimethyltricarballic acid, $\text{CO}_2\text{H}\cdot\text{CMe}_2\cdot\text{CH}(\text{CO}_2\text{H})\cdot\text{CH}_2\cdot\text{CO}_2\text{H}$,

obtained by hydrolysing the preceding ester with 10 per cent. hydrochloric acid, separates in small crystals melting at 155° ; when treated with a boiling solution of copper acetate, it yields a light blue precipitate which redissolves on cooling. The *imide*,



simultaneously produced during this hydrolysis, crystallises from water in colourless prisms and melts at $182-183^{\circ}$; it is a monobasic acid, readily hydrolysed by potassium hydroxide into the corresponding tricarballic acid.

G. T. M.

Interaction of Ammonium Cyanide with Acetone. By WLADIMIR VON GULEWITSCH (*Ber.*, 1900, 33, 1900—1901).—When acetone is left at the ordinary temperature with a freshly prepared 3 per cent. solution of ammonium cyanide (1 mol.) for 19 hours, and the solution subsequently boiled for 4 hours with dilute hydrochloric acid, 74 per cent. of the theoretical quantity of α -aminobutyric acid is obtained; when the mixture is left only $\frac{1}{2}$ hour at the ordinary temperature, the yield is very much diminished, although, according to Ljubawin (*Abstr.*, 1883, 178), these conditions are the most favourable in the case of the interaction of ammonium cyanide with aldehydes.

W. A. D.

Degradation of *d*-Galactose and of Lactose: *d*-Lyxose and Galactoarabinose. By OTTO RUFF and GERHARD OLLENDORFF (*Ber.*, 1900, 33, 1798—1810).—*d*-Lyxose (Fischer and Bromberg, *Abstr.*, 1896, i, 348; Wohl and List, *Abstr.*, 1898, i, 168) is readily prepared by oxidising calcium galactonate with hydrogen peroxide in presence of basic ferric acetate (compare Ruff, *Abstr.*, 1898, i, 516; 1899, i, 324, 869; 1900, i, 139); it forms colourless, transparent, hygroscopic, monoclinic crystals [$a:b:c = 1.6076:1:1.8277$, $\beta = 117^{\circ}50'$], sinters at 99° , melts at 101° (corr.), and shows mutarotation; an aqueous (?) solution, which 4 minutes after preparation had $[\alpha]_D - 3^{\circ}$, had $[\alpha]_D - 13.9^{\circ}$ after 24 hours. One part of *d*-lyxose dissolves in 37.97 parts of absolute alcohol, and 1 mg. reduces 1.793 mg. of copper according to Allihn's method. The sugar is not fermentable. *d*-Lyxosephenylbenzylhydrazone crystallises from 30 per cent. alcohol in slender, white needles, with H_2O , which melt at 116° ; from absolute alcohol, the anhydrous substance is obtained in hard prisms melting at 128° , whilst in the same solvent $[\alpha]_D + 26.39^{\circ}$. On reducing *d*-lyxose with sodium amalgam, *d*-arabitol (Ruff, *Abstr.*, 1899, i, 324) is obtained. The foregoing facts are in complete accord with Fischer's views as to the configuration of *d*-galactose, *d*-lyxose, and *d*-arabitol.

Lactobionic acid, on oxidation with hydrogen peroxide and ferric acetate, is transformed into a disaccharide, with 11 carbon atoms, to which the name *galactoarabinose* is given, since on hydrolysis with dilute sulphuric acid it yields *d*-arabinose and *d*-galactose; it forms a colourless, cupric-reducing, dextrorotatory syrup which could not be crystallised. The *osazone*, $\text{C}_{23}\text{H}_{30}\text{O}_8\text{N}_4$, crystallises from absolute alcohol, and melts when rapidly heated at $236-238^{\circ}$. The diphenylhydrazone could not be prepared, but the *phenylbenzylhydrazone*, $\text{C}_{24}\text{H}_{32}\text{O}_9\text{N}_2$, crystallises from 50 per cent. alcohol, and has $[\alpha]_D - 23.7^{\circ}$

in this solvent; it melts at 223° (corr.), and when treated with aqueous formaldehyde regenerates the disaccharide. The production of galactoarabinose from lactose by the foregoing method through lactobionic acid supports Fischer's contention (Abstr., 1888, 1267; 1889, 485) that the aldehyde group of lactose is present in the glucose portion of the molecule, and is not in agreement with the opposite conclusion recently arrived at by de Bruyn and Alberda van Ekenstein (Abstr., 1899, i, 661).

Galactosidogluconic acid, the synthetical product obtained from galactose and gluconic acid (Fischer and Beensch, Abstr., 1894, i, 565), is evidently not identical with lactobionic acid, since it fails to interact with hydrogen peroxide under the conditions already indicated; when action occurs on heating at $60-70^{\circ}$, galactoarabinose is not formed, but only *d*-galactose and *d*-arabinose along with glyoxal. The *dibenzylphenylhydrazone* of the latter, $C_{28}H_{26}N_4$, forms yellow needles and melts at 197.5° .
W. A. D.

Specific Heat of Wheat Starch as a Function of Hydration and Temperature. By HERMANN RODEWALD and A. KATTEIN (*Zeit. physikal. Chem.*, 1900, 33, 540—544).—The specific heats of wheat starch, containing from 0 to 33.6 per cent. of water, were determined at different temperatures. The temperature coefficients vary from 0.0006 to 0.0012, and the values at zero vary from 0.2697 to 0.3054, but not uniformly, as they first decrease, then increase, and again decrease with increasing hydration.
L. M. J.

Natural and Artificial Starch Grains. By HERMANN RODEWALD and A. KATTEIN (*Zeit. physikal. Chem.*, 1900, 33, 579—592).—If starch is brought into solution by heating with iodine at 130° , the iodine removed, and the starch precipitated from the solution, the resulting 'artificial' starch closely resembles pure starch grains in all its properties. By the method previously described by Rodewald (Abstr., 1898, ii, 61), the heat produced by soaking in water was determined for various varieties of starch, and a 'soluble amylose' at various degrees of hydrations. Curves and formulæ reproducing them are given, the differences between the various varieties being but slight. Osmotic measurements were made with starch iodide solution, membranes of parchment and of collodion being employed; these indicated values of 39,680 and 36,740 for the mol. weight of the starch. The artificial starch has a density 1.661, that of the wheat starch from which it was prepared being 1.6427. It dissolves in alkali, the solution being strongly dextrorotatory, the rotation being increased by addition of water, but decreased by more alkali, and in this respect it resembles the soluble amylose, the molecular rotation of the latter being, however, about 8 per cent. higher.
L. M. J.

"Swelling" (Quellung) and Wetting. By HERMANN RODEWALD (*Zeit. physikal. Chem.*, 1900, 33, 593—604).—On the assumption that the heat produced by the wetting or swelling of starch is due to an adhesive force between the starch and water, and is hence proportional to the surface, the author deduces an expression, $c(w_1 - w_0) = \log(r_0 + i)$

$-\log(r_1 + i)$ for the heat of swelling, where w_1 is the water content and r_1 the heat produced. The experimental data (preceding abstract) were in good accord with the values so calculated. The formula indicates that at a certain water concentration further addition should produce no heat effect, but it was found for all the varieties of starch examined that there was still a heat production of about 0.5 Cal. This is probably due to the supposition that the work of adhesion is proportional to the surface being inexact, as a second layer of water molecules is not in direct contact with starch. The surface area of the water molecules required per milligram of starch was estimated, and hence, assuming that each molecule of starch is surrounded by water molecules, the author calculates the molecular weight of the starch on the assumption (1) of cubic and (2) of spherical molecules, the numbers so obtained varying for the different varieties of starch from 103,300 to 17,430. L. M. J.

Galactosamine, a New Amino-sugar, as a Decomposition Product of the Gluco-proteid of the Albuminous Gland of the Frog. By FRIEDRICH N. SCHULZ and FRITZ DITTHORN (*Zeit. physiol. Chem.*, 1900, 29, 373—385).—This substance, described as a new amino-sugar, was obtained as a decomposition product of the gluco-proteid of the albuminous gland of the frog. The investigation is to be continued with other varieties of so-called mucin. W. D. H.

Halogen Derivatives of Hexamethylenetetramine. By M. HOEHNEL (*Arch. Pharm.*, 1900, 238, 163).—The author regrets having overlooked, in his recent papers (this vol., i, 279) a communication by Horton (Abstr., 1888, 1051) on the same subject. W. A. D.

The Thiocyanoacetic Acids. By GUSTAV FRERICHS and HEINRICH BECKURTS (*Arch. Pharm.*, 1900, 238, 9—15. Compare Claesson, Abstr., 1878, 37; Frerichs, Abstr., 1899, i, 796).—The salts, &c., obtained by Claesson from potassium thiocyanate and salts, &c., of chloroacetic acid are not all derivatives of thiocyanoacetic acid. The amide is derived from this acid, $\text{CN}\cdot\text{S}\cdot\text{CH}_2\cdot\text{CO}_2\text{H}$; the metallic salts and esters, however, from thiocarbimidoacetic acid, $\text{CS}\cdot\text{N}\cdot\text{CH}_2\cdot\text{CO}_2\text{H}$, whilst the free acid is a mixture of the two isomeric compounds. The thiocarbimido-derivatives are recognised as such by the fact that they yield hydrogen sulphide and hydrogen cyanide, but no thioglycollic acid, when boiled with alkalis; whereas the thiocyano-compounds yield thioglycollic acid, which is detected by acidifying with hydrochloric acid, adding a trace of ferric chloride and shaking with excess of ammonia, when a violet coloration is formed.

Thiocarbimidoacetamide, $\text{CS}\cdot\text{N}\cdot\text{CH}_2\cdot\text{CO}\cdot\text{NH}_2$, obtained by boiling potassium thiocyanate with chloroacetamide in alcoholic solution, melts at 115° ; cold aqueous ammonia transforms it into thiocyanoacetamide.

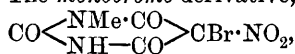
In a later communication (*ibid.*, 317—320), the authors state that they are in error as to the compound melting at 115° ; it had already been described by Miolati (Abstr., 1893, i, 405), who correctly regarded it as thiocyanoacetamide, whilst the product formed from it is thiohydantoin. Similarly, the compounds described by Frerichs (*loc. cit.*)

as thiocyanaceto-derivatives, are in reality the corresponding derivatives of thiohydantoin. C. F. B.

Cyanoselenium Compounds. By WILHELM MUTHMANN and E. SCHRÖDER (*Ber.*, 1900, 33, 1765—1769).—Potassium selenocyanide is best prepared by fusing pure potassium cyanide with selenium. Cyanogen triselenide is most advantageously obtained by the action of nitric oxide on a paste of potassium selenocyanide with water. Its mol. weight, determined by the boiling point method in benzene and in chloroform solution, corresponds with that required for the accepted formula $C_2N_2Se_3$. It acts vigorously on many organic compounds with production of selenium, but the exact course of the reaction has not been ascertained in any one case, as the products appear to be of a complex character. A. H.

Methylvioluric Acid and Methylidilituric Acid. By RUDOLF ANDREASCH (*Monatsh.*, 1900, 21, 281—300).—*Methylvioluric acid*, $CO<\begin{smallmatrix} NMe\cdot CO \\ NH-CO \end{smallmatrix}>C:N\cdot OH$, prepared from hydroxylamine hydrochloride and methylalloxan, crystallises, with H_2O , in slender needles which have a faint yellow tinge; it is moderately acid, decomposing carbonates and acetates, and forms violet-red coloured salts, which decompose when heated, evolving violet fumes; the *potassium*, *sodium* (with $1\frac{1}{2} H_2O$), *ammonium*, *calcium*, *barium*, *lead* (with $3H_2O$), *cadmium* (with $6H_2O$), *copper* (with $3H_2O$), and *zinc* (with H_2O) salts are described.

Methylidilituric acid, obtained by the oxidation of methylvioluric acid with nitric acid, crystallises from water in thick prisms which contain $1\frac{1}{2}H_2O$ and melt at 143° , and is not hydrolysed by alkalis. The *potassium*, *sodium* (with H_2O), *ammonium*, *barium* (with H_2O), *strontium* (with $3H_2O$), *lead* (with $2\frac{1}{2}H_2O$), and *cadmium* (with $2H_2O$) salts are described. The *monobromo-derivative*,



which crystallises in white, microscopic prisms melting at $138-139^\circ$, and *monochloro-derivative*, which crystallises in plates melting at 121° , were prepared. R. H. P.

Mercury Antimonide and Stibonium Compounds. By ALFRED PARTHEIL and E. MANNHEIM (*Arch. Pharm.*, 1900, 238, 166—184).—Although mercury antimonide cannot be prepared by passing hydrogen antimonide through solutions of mercuric chloride (compare Pfaff, *Ann. Phys. Chem.*, 1837, [i], 42, 344; Simon, *ibid.*, 566; Rose, *ibid.*, 1844, [i], 51, 423), it is formed quantitatively according to the equation $2SbH_3 + 3HgCl_2 = Sb_2Hg_3 + 6HCl$, when the carefully dried gas is passed through a mixture of dry mercuric chloride and sand contained in a rotating cylinder at the ordinary temperature; the action is, however, somewhat slow. The *antimonide*, Sb_2Hg_3 , is a dark-grey, heavy powder, which when pure is somewhat prone to decomposition, although quite stable when mixed with sand; with warm nitric acid, it yields mercuric nitrate and antimony tetroxide, whilst on heating, the mercury sublimes and the antimony burns to form the trioxide. With ethyl iodide at the temperature of boiling aniline, it yields *tetraethylstibonium mercuriodide*, $SbEt_4I\cdot HgI_2$, which

separates from alcohol in whitish-yellow crystals and melts at 93—95°. Tetraethylstibonium iodide, $\text{SbEt}_4\text{I} \cdot \frac{1}{3}\text{H}_2\text{O}$,* is very soluble in water, but crystallises from it in long needles which begin to decompose at 150°. The salt, $\text{SbEt}_4\text{Cl} \cdot 4\text{HgCl}_2$, crystallises from water in small, white octahedra, and melts at 141—142°; the aurichloride, $\text{SbEt}_4\text{Cl} \cdot \text{AuCl}_3 \cdot \frac{1}{2}\text{H}_2\text{O}$, forms yellow needles or plates, darkens at 150°, and melts at 178°; the platinichloride, $(\text{SbEt}_4)_2\text{PtCl}_6$, decomposes at 141°. The foregoing salts were also prepared from tetraethylstibonium iodide, obtained by Loewig and Schweitzer's method (*Annalen*, 1850, 75, 315, 338; 1856, 97, 322).

Tetrapropylstibonium mercuriodide, $\text{SbPr}^a_4\text{I} + \text{HgI}_2$, prepared either by the action of propyl iodide on mercury antimonide at 180°, or from *tetrapropylstibonium iodide*, SbPr^a_4I , obtained according to Loewig and Schweitzer's method (*loc. cit.*), crystallises from alcohol in lustrous, yellow prisms, and melts at 103·5°. The base, SbPr^a_4OH , forms long needles which are extremely hygroscopic.

Tetrapropylstibonium mercurichloride, $\text{SbPr}^a_4\text{Cl} \cdot \text{HgCl}_2$, crystallises from water in long, silky needles, from alcohol in thick prisms, and melts at 120—121°. The aurichloride, $\text{SbPr}^a_4\text{Cl} \cdot \text{AuCl}_3$, crystallises from 80 per cent. alcohol in beautiful, slender, yellow needles, and melts at 98°; the platinichloride, $(\text{SbPr}^a_4)_2\text{PtCl}_6$, crystallises from dilute hydrochloric acid in stout, yellowish-red octahedra, and melts and decomposes at 133°; the picrate, $\text{C}_{18}\text{H}_{30}\text{O}_7\text{N}_3\text{Sb}$, crystallises from 20 per cent. alcohol in small, yellow needles, and melts at 67·5°.

W. A. D.

Ring-system of Benzene. By HUGO KAUFFMANN (*Ber.*, 1900, 33, 1725—1742).—The nature of the ring-system in benzene derivatives can be ascertained to some extent by the action of Tesla-rays on their vapours. Luminescent substances are regarded as containing a ring prone to assume a quinone-like structure. Benzene and its homologues, diphenylmethane and dibenzyl, show practically no luminescence, whilst triphenylmethane is only slightly luminescent; naphthalene, anthracene, phenanthrene, acenaphthene, and chrysene are luminescent and are readily oxidised to quinones, and diphenyl, carbazole, and diphenylene oxide are also luminescent. The phenols are not luminescent, but catechol and resorcinol are slightly luminescent, and quinol and the trihydric phenols are strongly so, with the exception of pyrogallol, which does not contain a *p*-hydroxyl group and is only slightly luminescent; the phenol ethers are usually more luminescent than the phenols from which they are derived, although they are less readily oxidised to quinones. The amines are all luminescent, and more strongly so when alkylated, when two amino-groups are present or when a hydroxyl group is also present; tetrahydroquinoline and 1-methyltetrahydroquinoline are strongly luminescent, but not quinoline. Acetyl and benzylidene groups usually diminish the luminescence, and nitro-groups destroy it altogether, a result which is in accordance with the additional stability which they impart to the ring; chlorine also decreases it, bromine

* Loewig and Schweitzer describe tetraethylstibonium iodide with $1\text{H}_2\text{O}$.—W. A. D.

acts still more powerfully, whilst carboxylic acids and esters are usually entirely without luminescence.

It is remarkable that the quinones themselves, and all coloured benzene derivatives, are entirely non-luminescent; auxochromes increase the luminescence, chromophores decrease it. The leuco-compounds are, however, luminescent.

In the case of the phenazonium derivatives, the ring which will act as a quinone is that which contains luminescent groups, such as naphthalene in place of benzene or an amino- or hydroxyl group, and these groups increase the readiness with which substitution takes place; on the other hand, nitro-groups, &c., which decrease the luminescence, also protect the ring from attack. T. M. L.

Nitration of Nitrobenzene. By ARNOLD F. HOLLEMAN and B. R. DE BRUYN (*Rec. Trav. Chim.*, 1900, 19, 79—110. Compare this vol., i, 387).—A detailed account of a study of the nitration of nitrobenzene, made with a view of ascertaining (1) the relationship existing between the weights of the three isomerides produced; (2) the absolute value of the velocity constants of the reaction.

The relative proportions by weight of the three dinitrobenzenes are determined by a solubility method similar to that employed in the case of the nitrobenzoic acids (*Abstr.*, 1899, i, 282, 757; ii, 257). Dilute ethyl alcohol is employed as the solvent, and it is found that the solubility of any one of the dinitrobenzenes is not appreciably altered by the presence of its isomerides. The solution being saturated with two of the isomerides, the amount of the third present is indicated by the sp. gr. of the liquid, and tables and curves may be constructed by which the quantity of dissolved *o*- or *p*-dinitrobenzene may be readily determined, the amount of the *m*-compound being estimated by difference.

The following conclusions are derived from the quantitative study of the product of nitration: (1) The nitration of nitrobenzene to dinitrobenzene by anhydrous nitric acid at 0° or 30° is practically quantitative, whilst at 40° and in the presence of sulphuric acid there is a tendency to form trinitrobenzene. (2) An elevation of temperature causes an increase in the amounts of *o*- and *p*-dinitrobenzene produced. (3) Excess of concentrated sulphuric acid diminishes the production of *o*-dinitrobenzene, but increases that of the *p*-isomeride to approximately the same extent. (4) The presence of water causes a considerable alteration in the velocity of the reaction, but does not affect the proportion of the isomerides. (5) The three isomerides are produced in the same proportions by weight throughout the reaction.

The amount of dinitrobenzene produced after a given time is found by taking the sp. gr. of the mixture of this product with unaltered nitrobenzene, a table having been previously constructed showing the connection between the sp. gr. of the solution and the quantity of dissolved dinitro-compounds. The authors' experiments indicate that the nitration of nitrobenzene cannot be expressed in the simple mathematical form of a bimolecular reaction. The equation would only apply to the case of infinite dilution, and, moreover, the products of the reaction,

water and dinitrobenzene, exercise a very marked disturbing influence.
G. T. M.

General Method for Preparing Sulphonic Derivatives by Means of Disulphides. By J. J. BLANKSMA (*Rec. Trav. Chim.*, 1900, 19, 111—114. Compare this vol., i, 226).—A preliminary communication dealing with the action of an alcoholic solution of sodium disulphide on certain aromatic nitro-compounds. *o*-Chloronitrobenzene and its bromine analogue are readily converted into 1:1-dinitrodiphenyl disulphide, the latter substance, on oxidation, yielding *o*-nitrobenzenesulphonic acid. Sodium disulphide eliminates one atom of the halogen from 1:4:2-dichloronitrobenzene, 1:2:4-chlorodinitrobenzene, and the corresponding bromo-compounds, giving rise to aromatic disulphides which yield sulphonic acids on oxidation. Benzyl chloride and its *o*-nitro-derivative also yield disulphides, but these substances, when oxidised by nitric acid, are principally converted into carboxyl compounds. Allyl bromide and ethylene bromide also react with sodium disulphide, the compound derived from the latter yielding ethylenedisulphonic acid on oxidation. Sodium chloroacetate forms the disulphide $S_2(CH_2 \cdot CO_2Na)_2$, from which sulphoacetic acid may be prepared.
G. T. M.

The Number of Isomeric Naphthalene Derivatives. By HERMANN REY (*Ber.*, 1900, 33, 1910—1917).—This paper contains a complete list of the number of possible isomerides derivable from naphthalene by substitution of similar or dissimilar radicles for the hydrogen atoms.
J. J. S.

Action of Nitrous Acid on Ethyl Anilinomalonate. By RICHARD SYDNEY CURTISS (*Amer. Chem. J.*, 1900, 23, 509—512).—By the action of nitrous acid on ethyl anilinomalonate suspended in water, an amber-coloured oil is produced, to which the constitution $OH \cdot \overset{N}{\underset{NPh}{\curvearrowright}} C(CO_2Et)_2$ is assigned; it does not give Liebermann's nitroso-reaction, readily decomposes with loss of nitrous oxide, and has marked acid properties; the yellow, crystalline *potassium* salt decomposes at 118°, and the *sodium* salt at 118—122°. Acetic anhydride gave, in one instance, a substance melting at 114°, and of mol. wt. about 300, but in a second experiment a substance melting at 111° and of mol. wt. 222.
T. M. L.

Behaviour of Phenylcarbimide with Ethyl Acetoacetate. By WILHELM DIECKMANN (*Ber.*, 1900, 33, 2002—2005).—Ethyl acetoacetate reacts at the ordinary temperature with phenylcarbimide to form *ethyl acetylmalonanilate*, $NHPh \cdot CO \cdot CHAc \cdot CO_2Et$, which crystallises in colourless, glassy prisms or thick tablets melting at 57—58°. The formation of this compound from the ester throws some doubt on the trustworthiness of phenylcarbimide as a reagent for characterising the enolic form of tautomeric compounds.
R. H. P.

Constitution of Di-*p*-bromobenzylcyanamide. By C. LORING JACKSON and R. W. FULLER (*Amer. Chem. J.*, 1900, 23, 494—500).—*Di-p*-bromobenzylcyanamide, $CN \cdot N(CH_2 \cdot C_6H_4Br)_2$, prepared by the

action of *p*-bromobenzyl bromide on silver cyanamide, melts at 133°, crystallises from benzene in flat, white needles, dissolves in most organic solvents, but only slightly in water, shows a normal molecular weight in benzene solution by the cryoscopic method, does not form a salt with hydrogen chloride, and does not polymerise when heated alone, or with water, alkali hydroxides, or ammonia; it is not readily hydrolysed by hydrochloric acid, but with sulphuric acid it is converted to di-*p*-bromobenzylamine, ammonia, and carbon dioxide. The constitution of the cyanamide is thus established, and serves to confirm Fileti and Schiff's conclusion (*Annalen*, 1854, 90, 95) that the dialkylcyanamides are derived from $\text{NH}_2\cdot\text{CN}$, and not from $\text{NH}\cdot\text{C}\cdot\text{NH}$.
T. M. L.

Action of Cyanogen on Aromatic Amines. By WILHELM MEVES (*J. pr. Chem.*, 1900, [ii], 61, 449—476).—By the action of acetyl chloride on a solution in pyridine of the additive product, $\text{C}_{14}\text{H}_{14}\text{N}_2$, of cyanogen and aniline, a polymeric *acetyl* derivative, $\text{C}_{30}\text{H}_{30}\text{ON}_8$, is produced, which forms violet crystals, melts at 205—207°, forms salts with acids, dissolves in organic solvents, but not in water, and is somewhat unstable; the *hydrochloride*, $\text{C}_{30}\text{H}_{30}\text{ON}_8\cdot 2\text{HCl}$, is a dark, amorphous precipitate which has a slight dyeing power, and is reduced by iron filings and acetic acid to a leuco-compound which oxidises again on exposure to air. Benzoyl chloride gives an *anhydro-benzoyl* derivative, $\text{C}_{21}\text{H}_{16}\text{N}_4$, which crystallises from alcohol in minute, red needles, melts at 192—193°, has slight tinctorial properties, and is perhaps an imidazole derivative.

'Cyanosaniline' does not interact with ethyl orthoformate, and therefore probably does not contain a $-\text{NH}_2$ group. It has been prepared by the action of mercuric oxide on an alcoholic solution of aniline and dithio-oxamide, and identified by means of the acetyl and benzoyl derivatives already described. The amount of 'cyanotriphenylguanidine,' $\text{NPh}\cdot\text{C}\begin{smallmatrix} \text{NPh}\cdot\text{C}\cdot\text{NH} \\ \text{NPh}\cdot\text{C}\cdot\text{NH} \end{smallmatrix}$, obtained as a bye-product in the action of cyanogen on aniline, is only very small when the cyanogen is in excess.

'Cyano-*o*-toluidine' gives an *acetyl* derivative, $\text{C}_{34}\text{H}_{38}\text{ON}_8$, and *hydrochloride*, $\text{C}_{34}\text{H}_{38}\text{ON}_8\cdot 2\text{HCl}$, analogous to those derived from 'cyanosaniline.'

'Cyano-*p*-anisidine,' $[-\text{C}(\text{NH})\cdot\text{NH}\cdot\text{C}_6\text{H}_4\cdot\text{OMe}]_2$, prepared by the action of cyanogen on *p*-anisidine, crystallises from alcohol in silvery flakes, melts at 207—209°, and forms a *hydrochloride*, $\text{C}_{16}\text{H}_{18}\text{O}_2\text{N}_4\cdot 2\text{HCl}$; a *guanidine* derivative, $\text{C}_{24}\text{H}_{28}\text{O}_3\text{N}_5$, is also produced, which crystallises from alcohol in minute, yellow needles, melts with frothing at 154°, is a stronger base than the corresponding aniline derivative, and forms sparingly soluble red salts even with organic acids.

'Cyano-*o*-anisidine' crystallises in long prisms and melts at 205—207°; the *guanidine* derivative is only produced in small quantities, melts at 152°, and resembles the *o*-compound.

'Cyano-*p*-phenetidine,' $\text{C}_2(\text{NH})_2(\text{NH}\cdot\text{C}_6\text{H}_4\cdot\text{OEt})_2$, resembles 'cyanosanidine,' melts at 208—210°, and gives oxalophenetidide when acted on by nitrous acid; the yellow *guanidine* derivative, $\text{C}_{27}\text{H}_{29}\text{O}_3\text{N}_5$, melts

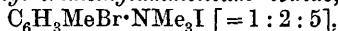
at 139—141°, forms a red *acetate* melting at 195—200°, and a red *hydrochloride*.

The only product of the action of cyanogen on β -naphthylamine is 'cyanotrinaphthylguanidine,' which is a yellow substance melting at 225—226°; it forms red salts, most of which are hydrolysed by adding much water; by boiling hydrochloric acid, it is hydrolysed into ammonia, β -naphthylamine, and oxalic acid.

'Cyanobenzidine' *platinichloride*, $(C_{26}H_{24}N_6)_2 \cdot H_2PtCl_6$, has been prepared and analysed, although all the salts are extremely unstable. When boiled with dilute sodium hydroxide, 'cyanobenzidine' is decomposed into benzidine, and a substance, $C_{14}H_{12}N_4$, which separates from toluene in white crystals, melts at 200°, and is regarded as 'dicyanobenzidine'; the further decomposition into benzidine, ammonia, and oxalic acid only takes place with difficulty.

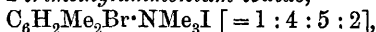
Dianisidine gives a red *compound*, $(C_{14}H_{16}O_2N_2)_2(CN)_2$, similar to 'cyanobenzidine.'
T. M. L.

Formation of Quaternary Ammonium Compounds in the case of Brominated Homologues of Aniline. By EMIL FISCHER and ADOLF WINDAUS (*Ber.*, 1900, 33, 1967—1975. Compare this vol., i, 224).—5-Bromo-o-tolyl trimethylammonium iodide,



crystallises from water in silky needles and decomposes at 178°. The 1 : 3 : 6-*compound* crystallises in flakes and decomposes at 176—177°. The 1 : 4 : 3-*compound* (Pesci, *Gazzetta*, 1898, 28, ii, 109) decomposes at 189—192°.

5-Bromo-p-xylyl-2-trimethylammonium iodide,



crystallises from water in four- or eight-sided flakes and decomposes at 188°. The 1 : 3 : 6 : 4-*compound* crystallises in long needles and decomposes at 200—201°. 5-Bromo-4-dimethylamino-*m*-xylene does not give a methiodide, in accordance with the rule that quaternary compounds are not formed where the two ortho-positions relatively to the amino-group are occupied. By the action of bromine on *as-m*-xylidine in presence of a large excess of cold hydrochloric or hydrobromic acid, a yellowish-red, crystalline mass is produced which has the composition $C_8H_{10}NBr \cdot HBr$, and probably contains a bromine atom in the amino-group, since the whole of the bromine is removed by sulphurous acid; on warming with hydrochloric acid, the bromine passes into the nucleus. 5-Bromo-1 : 3 : 4-xylidine (compare Vaubel, *Abstr.*, 1896, i, 646) crystallises from light petroleum in prisms and melts at 46—47°; the *acetyl* derivative crystallises from alcohol in prisms and melts at 197°; the constitution of the base has been established by converting it into a bromoxylene, which gave mesitylenic acid when acted on by sodium and ethyl chlorocarbonate. (4 or 5)-Bromo-1 : 3 : 2-xylidine, prepared in a similar way from the corresponding xyldine, crystallises from light petroleum in prisms and melts at 49—50°; the *acetyl* derivative crystallises from alcohol in prisms and melts at 197° (corr.); the bromine in the base is probably in the para-position to the amino-group, but this has not been proved.

Bromomesidine [$Me_3 : NH_2 : Br = 1 : 3 : 5 : 2 : 4$], prepared in a similar

way from mesidine, crystallises from light petroleum in transparent tablets and melts at 39°. In *p*-xylidine and the three toluidines, the method of brominating here described does not give such good results, and it is better to brominate the formyl or acetyl derivative. *Bromo-p-xylidine* crystallises from light petroleum in needles and melts at 96°; the *formyl* derivative crystallises from alcohol in long prisms and melts at 148°; the position of the bromine atom has not been determined.

T. M. L.

Quinquevalent Nitrogen. By WILHELM VAUBEL (*Ber.*, 1900, 33, 1713—1714).—A claim for priority (compare Lachman, this vol., i, 380).

T. M. L.

New Hydroxylamine Derivatives of Formic Acid. By GEORG SCHROETER and M. PESCHKES (*Ber.*, 1900, 33, 1975—1987. Compare Abstr., 1898, i, 623).—*α*-Benzylhydroxylamine, when heated with ethyl formate at 160° in sealed tubes, yields an oil boiling at 175—182° under 18 mm. pressure and benzaldoxime-O-benzyl ether. The sodium compound of benzaldoxime and *p*-nitrobenzyl chloride in alcoholic solution yield *benzaldoxime-p-nitrobenzyl ether*, which forms yellow crystals melting at 60—61°, and is not affected by hydrolytic agents. *p*-Chlorobenzylhydroxylamine hydrochloride, obtained by the action of hydrochloric acid on *p*-chlorobenzylacetoxime, which is formed by the action of *p*-chlorobenzyl chloride on sodium acetoxime, crystallises in silvery, thin leaflets, sublimes without melting, and, when mixed with a solution of potassium cyanate, forms *p*-chlorobenzyl-oxy-carbamide, which crystallises in white leaflets melting at 155—156°. The base, obtained by treating the hydrochloride with potassium hydroxide, boils at 127·4—128·2° under 17 mm. pressure and solidifies to a mass of hard, clear crystals, which melt at 38°. *p*-Bromobenzylhydroxylamine, obtained in an analogous manner to the chloro-derivative, boils at 133·5° under 10 mm. pressure, and crystallises in long, glassy needles which melt at 36—37°; *p*-bromobenzyl-oxy-carbamide melts at 157—158°; *p*-chlorobenzaldoxime *p*-chlorobenzyl ether and *p*-bromobenzaldoxime *p*-bromobenzyl ether, obtained as bye-products in the preparation of the above compounds, crystallise in colourless needles and melt respectively at 114° and 130°.

Formhydroxamoxime dibenzyl ether, $\text{CH}_2\text{Ph}\cdot\text{O}\cdot\text{N}\cdot\text{CH}\cdot\text{NH}\cdot\text{O}\cdot\text{CH}_2\text{Ph}$, obtained by the action of *α*-benzylhydroxylamine on formimidoether hydrochloride, crystallises in clusters of needles which melt at 42°, and forms a hydrochloride which is a colourless, microcrystalline powder. *Formhydroxamoxime di-p-chlorobenzyl ether*, obtained in a similar manner from *p*-chlorobenzylhydroxylamine, crystallises in small, lustrous, white needles which melt at 92·5—93·4°; it forms a colourless, crystalline hydrochloride and an acetyl derivative, which melts at 102—103·4°, and does not form a hydrochloride. *Formhydroxamoxime di-p-bromobenzyl ether* crystallises in small needles which melt at 100°, forms a colourless hydrochloride, and an acetyl derivative which crystallises in matted needles melting at 94—95°.

R. H. P.

Constitution of isoPurpuric Acid. By RUDOLF NIETZKI and WILHELM PETRI (*Ber.*, 1900, 33, 1788—1797).—*isoPurpuric acid* is

best prepared by the interaction of aqueous potassium cyanide with picric acid at a temperature not exceeding 35° , rather than at 100° as stated by Hlasiwetz (*Annalen*, 1859, 110, 289); the facts which follow show that it is a *dicyanopicramic acid* (4:6-dinitro-2-amino-3:5-dicyanophenol).

When dilute hydrochloric acid is added to potassium *isopurpurate* suspended in glacial acetic acid, the acid *potassium salt*, $C_8H_6O_6N_6K$, of *dicyanodinitrohydroxydiazobenzene*, $OH \cdot C_6(NO_2)_2(CN)_2 \cdot N:N \cdot OH$, separates in beautiful, golden needles, which can be dried at 100° without decomposition, but explode with great violence at about 210° ; on dissolving it in aqueous potassium carbonate, the normal *potassium salt*, $C_8O_6N_6K_2$, separates in brownish-yellow prisms; the acid *sodium salt*, $C_8HO_6N_6K$, and the normal *barium salt*, $C_8O_6N_6Ba + H_2O$, were also prepared. The parent substance, $C_8O_6N_6H_2$, separates in yellow needles on dissolving the foregoing salts in concentrated nitric acid; it is very soluble in water, and is remarkable in that it is only slightly explosive, and, unlike diazo-compounds, fails to condense with amines and phenols.

On reducing the foregoing diazo-salts in the cold with stannous chloride dissolved in dilute hydrochloric acid, slender, red needles of what is apparently the corresponding *hydrazine* are obtained, although the substance fails to give the usual hydrazine reactions; if the diazo-salts are reduced by a warm solution of stannous chloride in concentrated hydrochloric acid, 5-cyano-2:4:6-triamino-3-hydroxybenzamide is obtained, owing to one of the cyano-groups having undergone partial hydrolysis. The base yields a crystalline *hydrochloride*, which loses its hydrogen chloride completely on exposure to air; it is readily oxidised by manganese dioxide in alkaline solution to the *quinoneimide*, $NH \cdot C_6O(NH_2)_2(CN) \cdot CO_2H$, of *cyanodiaminobenzoic acid*; this forms dark yellow needles, yields copper-red, crystalline *sodium* and *potassium* salts, and is reduced by stannous chloride in hydrochloric acid to 5-cyano-2:4:6-triamino-3-hydroxybenzoic acid, which is sparingly soluble in water, is easily oxidisable, and was analysed in the form of its *triacetyl* derivative, $C_9H_5N_4O_3(OAc)_3$. The quinoneimide interacts with hydroxylamine to form an *oxime*, the *potassium salt* of which, $NH \cdot C_6(NH_2)_2(CO_2K)(CN) \cdot N \cdot OH + \frac{1}{2}H_2O$, forms dark red crystals, and, on reduction, yields 5-cyano-2:3:4:6-tetraminobenzoic acid, which rapidly oxidises in the air.

Attempts to hydrolyse the foregoing derivatives of *m*-cyanobenzoic acid to the corresponding *isophthalic acids* by means of hydrochloric or sulphuric acid failed. On warming the quinoneimide of cyanodiaminobenzoic acid, however, with aqueous potassium hydroxide on the water-bath and adding hydrochloric acid, the acid *potassium salt*, $C_8H_6O_6N_3K$, of the *quinoneimide* of *diaminoisophthalic acid*, $O \cdot C_6(NH_2)_2(CO_2H)_2 \cdot NH [= 1:2:6:3:5:4]$, is obtained as a vermilion, crystalline precipitate. The corresponding acid could not be isolated, since, on dissolving the salt in concentrated sulphuric acid, the *anhydride*, $C_8H_5O_4N_3$, separates in reddish-yellow crystals. On reduction with stannous chloride, the quinoneimide yields 2:4:6-triamino-5-hydroxyisophthalic acid, the *tetracetyl* derivative of which melts at 208° . On reducing the *oxime* of the quinoneimide of diamino-

isophthalic acid with stannous chloride and hydrochloric acid, *tetraminoisophthalic acid* is obtained, which reddens in the air, owing to oxidation occurring.

W. A. D.

Action of Nitric Acid on Trichloroguaiacol. By H. COUSIN (*Compt. rend.*, 1900, 131, 53—55. Compare this vol., i, 179).—Tetrachloroguaiacol, when treated with nitric acid, yields tetrachloro-o-quinone, and a similar result is obtained with tetrabromoguaiacol; the reaction with trichloroguaiacol takes an altogether different course.

The *quinone*, $C_{13}H_5O_4Cl_3$, is produced by the action of nitric acid on trichloroguaiacol dissolved in glacial acetic acid; it crystallises in reddish-yellow lamellæ melting at 158—162°, and separates from benzene solutions in prismatic crystals containing 1 mol. of the solvent. The corresponding *quinol*, $C_{13}H_7O_4Cl_3$, is readily obtained by the action of sulphurous acid on the quinone; it separates from benzene in colourless, prismatic crystals, which darken on exposure to the air and melt at 166—167°. Its alcoholic solution develops a green coloration with ferric chloride, the colour changing to violet on the addition of alkali. When subjected to Zeisel's method for the determination of methoxyl, the quinone yields 1 mol. of methyl iodide; on distilling it with zinc dust, diphenyl is obtained.

The reaction with nitric acid probably takes place in the following manner. Two mols. of trichloroguaiacol condense, losing 1 mol. of hydrogen chloride, one methyl group is removed by hydrolysis, and the product simultaneously undergoes oxidation. The quinone thus produced should have one or other of the following constitutions: $O:C_6Cl_3(OMe) \cdot C_6HCl_2(OH):O$ or $O:C_6HCl_2(OMe) \cdot C_6Cl_3(OH):O$.

G. T. M.

Synthesis of Dimethylmorphol and of isoMethylmorphol. By ROBERT PSCHORR and C. SUMULEANU (*Ber.*, 1900, 33, 1810—1823. Compare Vongerichten, this vol., i, 248).—*α-Phenyl-2-nitro-3:4-dimethoxycinnamic acid*, $NO_2 \cdot C_6H_2(OMe)_2 \cdot CH: CPh \cdot CO_2H$, is obtained when *o*-nitrovanillin methyl ether, melting at 55—56° (this vol., i, 178), is heated with anhydrous sodium acetate and acetic anhydride for some 24 hours; it crystallises from dilute alcohol in yellowish needles melting at 225° (corr.), and is sparingly soluble in ether, benzene, or chloroform. A small amount of 2-nitro-3:4-dimethoxystilbene is always obtained as a bye-product in the preparation of the cinnamic acid; it crystallises from hot alcohol in lemon-yellow, six-sided plates melting at 122—123°, and is readily soluble in ether, acetone, or hot acetic acid; it cannot be obtained directly from the acid by the elimination of carbon dioxide. *α-Phenyl-2-amino-3:4-dimethoxycinnamic acid*, obtained by reducing an ammoniacal solution of the nitro-acid with ferrous sulphate, crystallises in flat, yellowish prisms melting at 179° (corr.) and readily soluble in ether, acetone, acetic acid, chloroform, or hot benzene. When this acid is heated for some time with dilute sulphuric acid or more readily with acetic anhydride and a trace of sulphuric acid, it is converted into 2-phenyl-7:8-dimethoxycarbostyryl, which crystallises from hot toluene in colourless, flat needles melting at 247—248° (corr.). 3:4-Dimethoxyphenanthrene-9-carboxylic acid, formed when the

diazotised amino-acid is treated with molecular copper, crystallises from hot alcohol in small, yellowish needles melting at 227—228° (corr.); the *ferric* salt forms slender, yellow needles, and the *copper*, *lead*, and *mercuric* salts amorphous precipitates. When the acid is distilled under 300 mm. pressure, it is converted into 3:4-dimethoxyphenanthrene; this distils at 298—303° under 112 mm. pressure, crystallises from dilute alcohol in colourless, glistening, quadratic plates melting at 44°, and is in all respects identical with Vongerichten's dimethylmorphol (compare following abstract). The *picrate* forms ruby-red crystals melting at 105—106°, and the *dibromo-derivative*, $C_{16}H_{12}O_2Br_2$, needles melting at 124—125°.

When dimethylmorphol is hydrolysed with acetic and concentrated hydriodic acids, the product is not morphol, but 3-hydroxyphenanthrene; this crystallises in needles melting at 118—119°, and yields an *acetyl* derivative melting at 114—115°.

α-Phenyl-2-nitro-4-acetoxy-3-methoxycinnamic acid, obtained from *o*-nitroacetylvanillin, sodium phenylacetate, and acetic anhydride, crystallises from toluene in needles melting at 178° (corr.) and readily soluble in most organic solvents. The corresponding *amino-acid* could not be obtained in a pure state, as it is readily transformed into 3-phenyl-7-hydroxy-8-methoxy-2-carbostyryl, which crystallises in colourless needles melting at 243° (corr.). 3-Hydroxy-4-methoxyphenanthrene-9-carboxylic acid could not be obtained pure; it forms brown needles melting at 214—216° (corr.); when heated with 15 times its weight of glacial acetic acid at 210—215° for 10 hours, it yields 3-hydroxy-4-methoxyphenanthrene (*isomethylmorphol*) as an oil the *acetyl* derivative of which melts at 93—94°.

J. J. S.

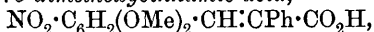
Identity of Dimethylmorphol and of 3:4-Dimethoxyphenanthrene. By EDUARD VONGERICHTEN (*Ber.*, 1900, 33, 1824—1825. Compare preceding abstract).—When acetylmethylmorphol is hydrolysed with sodium methoxide in the absence of air, and then heated with methyl iodide also in the absence of air, a dimethylmorphol is obtained which is identical with Pschorr's 3:4-dimethoxyphenanthrene.

J. J. S.

Synthesis of 4-Hydroxyphenanthrene. By ROBERT PSCHORR and BERNHARD JAECKEL (*Ber.*, 1900, 33, 1826—1829).—*α-Phenyl-2-nitro-3-methoxycinnamic acid*, $NO_2 \cdot C_6H_3(OMe) \cdot CH: CPh \cdot CO_2H$, obtained from 2-nitro-3-methoxybenzaldehyde (*Abstr.*, 1889, 1169), sodium phenylacetate, and acetic anhydride, crystallises in colourless plates melting at 226—227° (corr.), dissolves sparingly in toluene, and is insoluble in light petroleum; the *calcium*, *barium*, *mercuric*, *copper*, and *platinic* salts are described. The corresponding *amino-acid* crystallises from alcohol in lemon-yellow, felted needles melting at 208—209° (corr.), and is readily soluble in most organic solvents with the exception of light petroleum or water. The *ammonium*, *calcium*, and *silver* salts are described. When the acid is diazotised and treated with finely-divided copper, it yields 4-methoxyphenanthrene-9-carboxylic acid, which crystallises from toluene in slender needles melting at 224° (corr.), and only sparingly soluble in the usual solvents. 4-Methoxyphenanthrene, obtained by distilling the carboxylic acid

under 150 mm. pressure, crystallises from dilute alcohol in glistening plates melting at 68° ; it yields a *picrate*, $C_5H_{12}O, C_6H_3O_7N_3$, crystallising in red needles and melting at $187-188^{\circ}$ (corr.); when hydrolysed and heated with acetic anhydride, it yields 4-acetoxyphenanthrene, $C_{16}H_{12}O_2$, which crystallises from dilute alcohol in colourless plates melting at $58-59^{\circ}$. 4-Methoxydibromophenanthrene, $C_{15}H_{10}OBr_2$, crystallises in colourless needles melting at 152° (corr.), and 4-methoxydibromophenanthraquinone, $C_{15}H_8O_3Br_2$, crystallises in reddish-yellow needles melting at 160° .
J. J. S.

Synthesis of 2:3-Dimethoxyphenanthrene. By ROBERT PSCHORR and WALTER BUCKOW (*Ber.*, 1900, 33, 1829—1832).—*a*-Phenyl-2-nitro-4:5-dimethoxycinnamic acid,



obtained by the condensation of sodium phenylacetate, *s*-nitrovanillin methyl ether, and acetic anhydride, crystallises from alcohol in yellow, felted needles melting at 219° (corr.); it dissolves readily in most organic solvents, sparingly in benzene or ether, and is practically insoluble in light petroleum. The *silver*, *lead*, *platinum*, *copper*, and *ferric* salts are described. The corresponding amino-acid crystallises from alcohol in yellow, hair-like needles melting at 209° (corr.), and is insoluble in water or light petroleum; its *hydrochloride*, *nitrate*, and *sulphate* crystallise in needles, and the sulphate is somewhat sparingly soluble. When the amino-acid is heated with acetic anhydride and a little sulphuric acid, it is converted into its inner anhydride, 2-phenyl-5:6-dimethoxy-1-carbostyryl, which crystallises from alcohol in long, colourless needles melting at 261° (corr.).

2:3-Dimethoxyphenanthrene-9-carboxylic acid, formed when the amino-acid is diazotised and treated with copper powder, crystallises from alcohol in needles melting at 270° (corr.), and is insoluble in water or light petroleum; its *silver*, *barium*, *lead*, and *platinum* salts form colourless, amorphous precipitates. When the acid is distilled under 150—200 mm. pressure, a 40—45 per cent. yield of 2:3-dimethoxyphenanthrene is obtained; this crystallises from dilute alcohol in plates melting at 131° (corr.), and is readily soluble in most organic solvents. The *picrate* forms long, yellowish-red needles melting at $127-128^{\circ}$, and is readily soluble in alcohol. Dimethoxydibromophenanthrene, $C_{16}H_{12}O_2Br_2$, crystallises from acetic acid in needles melting at 160° (corr.).

2:3-Dimethoxyphenanthraquinone forms dark red needles melting at 304° (corr.), and dimethoxydibromophenanthraquinone brownish-yellow crystals melting at 158° .
J. J. S.

An Aromatic Alcohol in German Oil of Roses. By HUGO VON SODEN and WILHELM ROJAHN (*Ber.*, 1900, 33, 1720—1724).—On distilling the blossoms with water, oil of roses and 'rose-water' are obtained, and the latter is redistilled to obtain a further quantity of oil of roses, leaving behind an aqueous residue. By extracting this residue with ether, an oil was obtained (200 grams from 800 kilograms of the water) which was found to consist of benzylcarbinol (β -phenylethyl alcohol); when oxidised with chromic acid, this gave as the chief product β -phenylethyl phenylacetate, $CH_2Ph \cdot CO_2 \cdot CH_2 \cdot CH_2Ph$, which

crystallises from methyl alcohol in long needles, melts at 28° , boils at 330° with slight decomposition, and is hydrolysed by alcoholic potash to phenylacetic acid.

By a similar method, the presence of phenylethyl alcohol was detected in 'rose-water,' and, in smaller quantities, in German oil of roses. The alcohol was prepared by Radziszewski (Abstr., 1876, ii, 78) by reducing phenylacetaldehyde with sodium amalgam, but a better yield is obtained by reducing with zinc dust and acetic acid; the pure alcohol boils at 219° , has a sp. gr. 1.0235 at 15° , and is oxidised to the ether melting at 28° . T. M. L.

***o*-Methoxyphenyltrichloromethylcarbinol.** By S. LEBEDEF (J. Russ. Phys. Chem. Soc., 1900, 32, 197—207).—*o*-Methoxyphenyltrichloromethylcarbinol, $\text{CCl}_3\cdot\text{CH}(\text{OH})\cdot\text{C}_6\text{H}_4\cdot\text{OMe}$, formed by the action of potassium hydroxide and chloroform on *o*-methoxybenzaldehyde, is obtained either as glistening crystals melting at 53° , or as a thick, reddish-yellow liquid boiling at 174° under 12 mm. pressure, which has a sp. gr. 1.4473 at $0^{\circ}/0^{\circ}$, dissolves readily in ether and slightly in light petroleum, and absorbs moisture from the air with development of a brownish coloration. Its acetyl derivative, $\text{C}_{11}\text{H}_{11}\text{O}_3\text{Cl}_3$, separates from alcohol in well-developed, monoclinic crystals melting at 58° and exhibiting prismatic hemihedrism [$a:b:c = 0.9370:1:0.6036$, $\beta = 98^{\circ}48'$]. The acute bisectrix makes an angle of about 22.5° with the a axis and about 14.5° with the c axis; the crystals are optically negative and show horizontal dispersion, $\rho > v$. By treating an alcoholic solution of this acetyl derivative with zinc, two products are obtained:

(1) *β -Dichloro-*o*-methoxystyrene*, $\text{CCl}_2\cdot\text{CH}\cdot\text{C}_6\text{H}_4\cdot\text{OMe}$, is a colourless liquid with a pleasant, though weak, odour; it boils at 123 — 125° under 12 mm. pressure, and has a sp. gr. 1.2899 at $0^{\circ}/0^{\circ}$ and 1.2701 at $20^{\circ}/0^{\circ}$.

(2) *Acetyl-*o*-methoxyphenyldichloromethylcarbinol*,
 $\text{CHCl}_2\cdot\text{CH}(\text{OAc})\cdot\text{C}_6\text{H}_4\cdot\text{OMe}$,

separates from ether in crystals melting at 108° , and has the normal molecular weight in freezing benzene.

o-Methoxyphenylacetic acid, $\text{OMe}\cdot\text{C}_6\text{H}_4\cdot\text{CH}_2\cdot\text{CO}_2\text{H}$, prepared by the action of alcoholic potash (4 mols.) on *o*-methoxydichlorostyrene (1 mol.), separates from ether in crystals which melt at 123° and are readily soluble in boiling water. T. H. P.

Synthesis of Styryltrichloromethylcarbinol and the Action of 5 per cent. Aqueous Potassium Hydroxide on it. By A. DRBOGLAFF (J. Russ. Phys. Chem. Soc., 1900, 32, 216—230).—*Styryltrichloromethylcarbinol*, $\text{CCl}_3\cdot\text{CH}(\text{OH})\cdot\text{CH}:\text{CHPh}$, obtained by the action of potassium hydroxide and chloroform on cinnamaldehyde, crystallises from light petroleum in bushy aggregates of slender needles melting at 67° ; it dissolves readily in ether, alcohol, chloroform, benzene, or carbon disulphide, less so in light petroleum, and is completely insoluble in water. By heating with water in sealed tubes at 180° , it yields β -benzoylpropionic acid. Its acetyl derivative, $\text{C}_{12}\text{H}_{11}\text{O}_2\text{Cl}_3$, is a thick, faintly-yellow liquid boiling at 160 — 165° under 20 mm. pressure. By the action of cold 5 per cent. aqueous potassium hydroxide, styryltrichloromethylcarbinol is converted into

β -benzoylpropionic acid which, when heated in molecular proportion with phenylhydrazine, gives the anhydride of its phenylhydrazone, obtained by Fittig (*Annalen*, 1898, 299, 28).

With a cold 5 per cent. solution of sodium ethoxide, styryltrichloromethylcarbinol yields *phenylallenecarboxylic acid*, $\text{CHPh}:\text{C}:\text{CH}\cdot\text{CO}_2\text{H}$, which was obtained as a pale yellow resin; the *silver* salt was prepared. On treatment with cold 5 per cent. aqueous potassium hydroxide, this acid is converted into β -benzoylpropionic acid; it may hence be regarded as an intermediate product in the transformation of styryltrichloromethylcarbinol into β -benzoylpropionic acid by means of cold potassium hydroxide solution. T. H. P.

Action of Anhydrous Nitric Acid on the Isomeric Chlorobenzoic Acids and their Derivatives. By P. J. MONTAGNE (*Rec. Trav. Chim.*, 1900, 19, 46—78. Compare Taverne, *Abstr.*, 1898, i, 525, 586, 658, and Holleman, this vol., i, 387).—The *methylamide* of *o*-chlorobenzoic acid crystallises from dilute alcohol in monoclinic plates and melts at $121\cdot5^\circ$; the *dimethylamide* is a liquid at the ordinary temperature, it boils at $157\cdot5$ — 159° under 14 mm. pressure, and solidifies at $13\cdot5^\circ$. 2-Chloro-5-nitrobenzoic chloride boils at 157 — 158° under 11 mm. pressure; the *methyl* ester of the corresponding acid crystallises from methyl alcohol in monoclinic needles and melts at 73° ; the *amide* forms monoclinic needles melting at 178° , the *methylamide* and *dimethylamide* melt at 174° and $124\cdot5^\circ$ respectively.

The *methylamide* of *m*-chlorobenzoic acid crystallises from dilute alcohol in monoclinic needles melting at 75° , and separates from aqueous solutions in needles containing 1 mol. of the solvent; the *dimethylamide* forms rhombic plates and melts at 61° . 3-Chloro-6-nitrobenzoic chloride boils at 167° under 17 mm. pressure, the corresponding *methyl* ester crystallises from methyl alcohol in monoclinic plates and melts at $48\cdot5^\circ$; the *amide* forms triclinic needles melting at 154° ; the *methylamide* crystallises in white needles and melts at 134° ; the *dimethylamide* melts at $104\cdot5^\circ$. The *methylamide* of *p*-chlorobenzoic acid forms monoclinic needles and melts at 161° , the *dimethylamide*, crystallising in a similar form, melts at 59° .

4-Chloro-3-nitrobenzoic chloride melts at 51° and boils at 170 — $170\cdot5^\circ$ under 22 mm. pressure; the corresponding *methyl* ester forms white, monoclinic needles melting at 83° ; the *amide* melts at 156° , the *methylamide* at $135\cdot5^\circ$, and the *dimethylamide* at $113\cdot5^\circ$.

The methyl *o*-, *m*-, and *p*-chlorobenzoates, on nitration with anhydrous nitric acid at 0° , yield respectively the methyl 2:5-, 3:6-, and 4:3-chloronitrobenzoates. Under similar conditions, the *o*-, *m*-, and *p*-chlorobenzamides are converted respectively into 2:5-, 3:6-, and 4:3-chloronitrobenzamides, the ortho-compound being more readily nitrated than its isomerides. The nitration of the methylamides and dimethylamides of the chlorobenzoic acids at 0° gives rise to nitroderivatives containing the entering group in the same position as in the preceding examples, but in addition the *m*- and *p*-methylamides also yield methylnitramines, $\text{NO}_2\cdot\text{C}_6\text{H}_3\text{Cl}\cdot\text{CO}\cdot\text{NMe}\cdot\text{NO}_2$, the *m*-compound decomposing at 148° and the *p*-isomeride at 90° ; these nitramines

may also be prepared by the direct action of nitric acid on the corresponding chloronitromethylamides. When the nitration of the chlorobenzamides is carried out at the ordinary temperature, the nitrated amides first produced undergo hydrolysis and yield the corresponding chloronitrobenzoic acids; the methylamides undergo a similar change, giving rise to these nitrated acids, nitrous oxide, and methyl nitrate, whilst the dimethylamides also give rise to the same acids and dimethylnitramine. The orientation of the nitro-derivatives obtained as the chief products of the above-mentioned reactions is the same as that of the chloronitrobenzoic acids produced by the direct nitration of the chlorobenzoic acids.

G. T. M.

Intramolecular Rearrangement. By KARL AUWERS (*Ber.*, 1900, 33, 1923—1924. Compare Einhorn, this vol., i, 439).—*Dibromo-o-hydroxybenzylacetylanilide*, $\text{OH} \cdot \text{C}_6\text{H}_2\text{Br}_2 \cdot \text{CH}_2 \cdot \text{N}(\text{Ac})\text{Ph}$ [$\text{OH} : \text{Br}_2 : \text{CH}_2 = 1 : 4 : 6 : 2$], is obtained when the acetyl derivative of dibromo-*o*-hydroxybenzyl bromide (*Annalen*, 1898, 302, 150) is warmed with aniline; it melts at 152° , is soluble in cold dilute alkalis, and may also be obtained by the action of acetic anhydride on dibromo-*o*-hydroxybenzylaniline. The isomeric meta- and para-compounds do not undergo similar changes.

J. J. S.

Sodium Salts of the Amides. By HENRY L. WHEELER (*Amer. Chem. J.*, 1900, 23, 453—471).—The amount of sodium salt formed by the action of sodium amalgam on a solution of an amide in boiling benzene does not depend in any regular way on the affinity constants of the acid and base from which the amide is derived. A disubstituted formamide gives a sodium derivative less readily than a mono-substituted formamide, and the inhibiting effect of a radicle is greater when it is attached to the CO group than when it is attached to the NH group, suggesting that the sodium of the salts is associated with oxygen and not with nitrogen. In contrast to oxindole and phthalimidine, benzoylbenzylamine is quite inert.

o-Toluamide forms a sodium salt somewhat less readily than benzamide, but trimethylbenzamide is only slightly less active in this respect than *o*-toluamide. As regards substitution in the amino-group, benzylbenzamide, methylbenzamide, and ethylbenzamide are practically inert, but benzanilide gives a considerable amount of sodium derivative.

Sodium derivatives of the following *amides* have been prepared and analysed; oxanilide, benzamide, oxindole, phthalimidine, *o*-formyltoluidide, *o*-toluamide, α -formylnaphthalide, α -naphthamide, 2 : 4 : 6-trimethylformylanilide, 2 : 4 : 6-trimethylbenzamide, and 2 : 4 : 6-tribromobenzamide.

It is suggested that the formation of sodium derivatives is conditioned by the presence of a trace of moisture and that an additive compound with sodium hydroxide is formed as an intermediate product; three such additive compounds have been prepared. 2 : 4 : 6-*Trimethylbenzamide potassium hydroxide* was prepared by shaking an ethereal solution of the amide with powdered potassium hydroxide; it is completely decomposed by water. 2 : 4 : 6-*Tribromobenzamide sodium hydroxide*, $\text{C}_6\text{H}_2\text{Br}_3 \cdot \text{CO} \cdot \text{NH}_2 \cdot \text{NaOH}$, was prepared by the action of

powdered sodium hydroxide on a solution of the amide in benzene, and is completely decomposed by water; the chloride, methyl ester, and dimethylamide do not combine with caustic alkalis.

Thioacetanilide sodium hydroxide, $\text{CSPH}\cdot\text{NH}_2\cdot\text{NaOH}$, was prepared in a similar manner, and when acted on by benzoyl chloride gave acetanilide and thiobenzoic acid, showing that it is probably a derivative of the formula $\text{NHPh}\cdot\text{CMe}(\text{OH})\cdot\text{SNa}$, and not a mere 'molecular compound.'
T. M. L.

Action of Benzyl Cyanide on Ethyl Cinnamate. By EMIL ERLÉNMEYER, jun. (*Ber.*, 1900, 33, 2006—2011).—The experiments of Walther and Schickler (*Abstr.*, 1897, i, 524) on the condensation of benzyl cyanide and ethyl cinnamate in the presence of sodium ethoxide have been repeated, and two new compounds isolated; one of these has the empirical formula $\text{C}_{19}\text{H}_{19}\text{O}_2\text{N}$, and crystallises in small, colourless needles melting at $99-100^\circ$, and the other has the formula $\text{C}_{28}\text{H}_{25}\text{O}_3\text{N}$, and crystallises in small, colourless needles melting at $206-207^\circ$. The paper concludes with a discussion of the probable formulæ of these compounds.
R. H. P.

New Drugs. Glycinyll Derivatives of the Esters of Aromatic Amino- and Hydroxyamino-acids. By ALFRED EINHORN and MAX OPPENHEIMER (*Annalen*, 1900, 311, 154—178. Compare this vol., i, 439).—*Methyl chloroacetylanthranilate*, $\text{CH}_2\text{Cl}\cdot\text{CO}\cdot\text{NH}\cdot\text{C}_6\text{H}_4\cdot\text{CO}_2\text{H}$, crystallises from absolute alcohol in slender needles and melts at $98-99^\circ$. *Methyl chloroacetyl-m-aminobenzoate* forms pale brown crystals and also melts at $98-99^\circ$. *Methyl chloroacetyl-p-aminobenzoate* separates from alcohol in white crystals and melts at 138° .

Methyl chloroacetyl-m-aminocinnamate,
 $\text{CH}_2\text{Cl}\cdot\text{CO}\cdot\text{NH}\cdot\text{C}_6\text{H}_4\cdot\text{CH}\cdot\text{CH}\cdot\text{CO}_2\text{Me}$,
crystallises in small needles and melts at 122° . *Methyl chloroacetyl-p-aminocinnamate* forms lustrous, pale brown needles and leaflets melting at $155-156^\circ$.

Methyl 3-chloroacetylamino-o-hydroxybenzoate,
 $\text{CH}_2\text{Cl}\cdot\text{CO}\cdot\text{NH}\cdot\text{C}_6\text{H}_3(\text{OH})\cdot\text{CO}_2\text{Me}$,
crystallises in slender needles and melts at 106° .

5-Chloroacetylamino-o-hydroxybenzoic acid, $\text{C}_9\text{H}_8\text{O}_4\text{NCl}\cdot\text{H}_2\text{O}$, crystallises from glacial acetic acid in nodules and melts at $233-234^\circ$, when it decomposes; the *methyl* and *ethyl* esters melt at 157° and 131.5° respectively.

Methyl 4-chloroacetylamino-m-hydroxybenzoate melts at $187-188^\circ$, and *methyl 3-chloroacetylamino-p-hydroxybenzoate* melts at $191-192^\circ$.

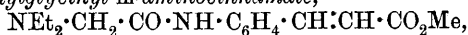
Methyl methylglycinyllanthranilate, $\text{NHMe}\cdot\text{CH}_2\cdot\text{CO}\cdot\text{NH}\cdot\text{C}_6\text{H}_4\cdot\text{CO}_2\text{Me}$, is a yellow oil yielding a crystalline *hydrochloride* which melts at 202° . *Methyl ethylglycinyllanthranilate* is also an oil; the *hydrochloride*, which crystallises from acetone, melts at 191° , when it decomposes. The *hydrobromide* of methyl dimethylglycinyllanthranilate melts and decomposes at 195° ; the *hydrobromide* of methyl diethylglycinyllanthranilate melts at 120° .

Methyl ethylglycinyll-m-aminobenzoate melts at $68-69^\circ$; the *hydrochloride* crystallises in small needles and melts at $193-194^\circ$. *Methyl*

diethylglycinyll-m-aminobenzoate is an oil yielding the *hydrochloride* which melts at 177°.

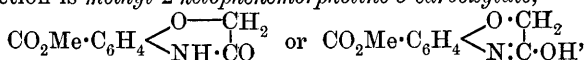
Methyl methylglycinyll-p-aminobenzoate crystallises from ethyl acetate in slender needles and melts at 108—109°; the *hydrochloride* melts at 225—226°. *Methyl ethylglycinyll-p-aminobenzoate* melts at 101—102°, and the *hydrochloride* at 218°. *Methyl diethylglycinyll-p-aminobenzoate* melts at 59—60°, the *hydrochloride* at 186—187°, and the *hydrobromide* at 170·5°.

Methyl diethylglycinyll-m-aminocinnamate,



is an oil forming the *hydrochloride*, which melts at 165°. *Methyl diethylglycinyll-p-aminocinnamate* is also an oil, yielding the *hydrochloride*, which crystallises in needles and melts at 188—189°.

Methyl p-diethylglycinyllamino-m-hydroxybenzoate, prepared from methyl *p*-chloroacetyl-amino-*m*-hydroxybenzoate (*chloroacetylorthoform*) and diethylamine, crystallises from dilute alcohol in leaflets, and melts at 157—158°; the *hydrochloride* melts at 95—96°. The other product of the action is *methyl 2-ketophenemorpholine-5-carboxylate*,



which crystallises from glacial acetic acid in slender needles, dissolves sparingly in most solvents, and melts at 253°; the *acid* melts at 290°, and the *amide* at 270°.

Methyl m-diethylglycinyllamino-p-hydroxybenzoate, prepared from methyl *m*-chloroacetyl-amino-*p*-hydroxybenzoate and diethylamine, crystallises from acetone in slender, lustrous leaflets and melts at 174·5°; the *hydrochloride* is very hygroscopic, and, after softening at 60—80°, melts at 162°. *Methyl 2-ketophenemorpholine-6-carboxylate* is also produced, and melts at 193—194°; the *acid* melts at 285°, and the *amide* crystallises in small, white leaflets.

Methyl 3-diethylglycinyllaminosalicylate, obtained from methyl 3-chloroacetyl-amino-*o*-hydroxybenzoate and diethylamine, melts at 41—42°, and yields the *hydrochloride* melting at 75—76°. There is also produced *methyl 2-ketophenemorpholine-4-carboxylate*, which crystallises from methyl alcohol in needles and melts at 200—201°.

Methyl 5-methylglycinyllaminosalicylate melts at 73—74°, and the *hydrochloride* melts and decomposes at 220°. *Methyl 5-ethylglycinyllaminosalicylate* melts at 58—59°, and the *hydrochloride* at 225·5°. *Methyl 5-diethylglycinyllaminosalicylate* (*nirvanine*) is a yellow oil forming a crystalline *hydrochloride* which melts and decomposes at 185°; the *aureichloride*, *platinichloride*, and *mercurichloride* contain 1H₂O, and melt at 170—171°, 210°, and 150—151° respectively. The *amide* crystallises from benzene in white needles and melts at 144°. *Ethyl 5-diethylglycinyllaminosalicylate* is an oil, and yields the *hydrochloride*, which melts at 198·5°, and in aqueous solution develops a violet coloration with ferric chloride.

M. O. F.

Alkylthiosulphonated Ethyl Acetoacetate. By JULIUS TROEGER and ERICH EWERS (*Arch. Pharm.*, 1900, 238, 309—320).—Thiosulphonates do not condense easily with chloroketones, but readily interact with ethyl α -chloroacetoacetate. Potassium

benzenethiosulphonate forms *ethyl phenylthiosulphonacetate*, $\text{SO}_2\text{Ph}\cdot\text{S}\cdot\text{CHAc}\cdot\text{CO}_2\text{Et}$, which separates from alcohol in compact, white crystals and melts at $55-56^\circ$. *Ethyl p-tolylthiosulphonacetate* separates from alcohol in large, glistening tablets and melts at $62-63^\circ$.

Ethyl β -naphthylthiosulphonacetate separates from alcohol in well-formed crystals and melts at 82° . The α -naphthyl compound separates from methyl alcohol in compact, glistening crystals and melts at $89-90^\circ$. All these compounds give a blood-red coloration with ferric chloride. T. M. L.

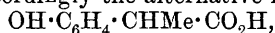
Oxidation of Anethole and Analogues (*isoSafrole*, *iso-Apiole*, &c.) containing Propenylic Side Chains. By J. BOUGAULT (*Compt. rend.*, 1900, 130, 1766-1768).—The *aldehyde*, $\text{C}_{10}\text{H}_{12}\text{O}_2$, obtained by oxidising anethole in alcoholic solution with a mixture of mercuric oxide and iodine, is a colourless, highly refractive, inodorous liquid, volatile in steam and boiling at $252-254^\circ$; it is almost insoluble in water or light petroleum, but dissolves readily in alcohol, ether, or chloroform.

The *acid*, $\text{C}_{10}\text{H}_{12}\text{O}_3$, produced by shaking the aldehyde with moist silver oxide in the presence of sodium hydroxide solution, melts at 57° .

Since these substances result from the oxidation of the propenylic side chain of anethole, their constitutions may be represented provisionally by the following formulæ: $\text{OMe}\cdot\text{C}_6\text{H}_4\cdot\text{C}_2\text{H}_4\cdot\text{CHO}$ and $\text{OMe}\cdot\text{C}_6\text{H}_4\cdot\text{C}_2\text{H}_4\cdot\text{CO}_2\text{H}$.

The *acids*, $\text{C}_{10}\text{H}_{10}\text{O}_4$, $\text{C}_{14}\text{H}_{14}\text{O}_4$, and $\text{C}_{12}\text{H}_{14}\text{O}_6$, obtained by similar processes from *isosafrole*, *isomethyleugenol*, and *isoapiole* melt at 80° , 60° , and 97° respectively. G. T. M.

Methoxyhydratropic Acid obtained by Oxidising Anethole; Identity of Phloretic and Hydroparacoumaric Acids. By J. BOUGAULT (*Compt. rend.*, 1900, 131, 42-45. Compare preceding abstract).—Hydroparacoumaric acid has the constitution $\text{OH}\cdot\text{C}_6\text{H}_4\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{CO}_2\text{H}$, having been synthesised from *p*-aminocinnamic acid, and accordingly the alternative formula,



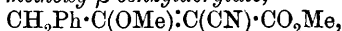
has hitherto been assigned to phloretic acid, its supposed isomeride. A comparative study of the derivatives of these acids shows unmistakably that the two substances are identical. It follows that their methyl derivatives, methoxyparacoumaric acid and methylphloretic acid, are also identical, having the formula $\text{OMe}\cdot\text{C}_6\text{H}_4\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{CO}_2\text{H}$; the alternative formula, $\text{OMe}\cdot\text{C}_6\text{H}_4\cdot\text{CHMe}\cdot\text{CO}_2\text{H}$, is therefore available for the new isomeric acid obtained by the author in oxidising anethole, and, accordingly, this compound is *methoxyhydratropic acid*; its aldehyde, formed as an intermediate product in the oxidation, consequently has the formula $\text{OMe}\cdot\text{C}_6\text{H}_4\cdot\text{CHMe}\cdot\text{CHO}$.

It is difficult to interpret these results on the assumption that anethole contains the straight chain $\cdot\text{CH}\cdot\text{CHMe}\cdot$; if, however, this substituent group is a trimethylene residue, $\cdot\text{CH}\cdot\begin{smallmatrix} \text{CH}_2 \\ | \\ \text{CH}_2 \end{smallmatrix}$, then a simple explanation of the oxidation becomes possible.

These remarks apply also to the acids and aldehydes derived from *isosaftrole*, *isomethyleugenol*, and *isoapiole*. G. T. M.

Alkyl Salts of α -Cyano- β -alkyloxy- β -phenyl- and - β -benzyl-acrylic Acids. By ALBIN HALLER and G. BLANC (*Compt. rend.*, 1900, 130, 1591—1595).—*Ethyl α -cyano- β -methoxy- β -phenylacrylate*, $\text{OMe} \cdot \text{CPh} : \text{C}(\text{CN}) \cdot \text{CO}_2\text{Et}$, obtained by the action of methyl iodide on ethyl argentocyanobenzoylacetate in presence of ether, forms white crystals which melt at 106 — 107° . The corresponding *β -ethoxy-acid* forms triclinic crystals which melt at 86° , and the *β -propoxy-acid* forms white crystals which melt at 95 — 96° . All three acids, when dissolved in alcohol and mixed with aqueous ammonia, yield one and the same amino-derivative, crystallising in white crystals melting at 125° , the amino-group having displaced the alkyloxy-group.

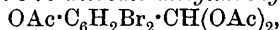
Methyl α -cyano- β -methoxy- β -benzylacrylate,



and the corresponding *β -ethoxy-acid*, are oily compounds obtained by the action of methyl and ethyl iodides respectively on methyl argentocyanacetophenylacetate, and when treated with ammonia they both yield the same white, crystalline amino-derivative melting at 101 — 102° , in which the alkyloxy-group has been displaced by the amino-group.

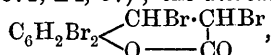
It would seem that, in the form of argento-derivatives, the alkyl salts of benzoyl and cyanoacetyl-phenylacetic acids behave like argento-derivatives of the alkyl acetoxyacetates, the group $\cdot \text{CO}(\text{CN}) \cdot \text{CH} \cdot \text{CO}_2\text{R}$ taking the form $\cdot \text{C}(\text{CN})(\text{OH}) : \text{C} \cdot \text{CO}_2\text{R}$, and the tautomerism being determined by the introduction of silver into the molecule. C. H. B.

Tribromocoumarin and its Derivatives. II. By HUGO SIMONIS and G. WENZEL (*Ber.*, 1900, 33, 1961—1967. Compare this vol., i, 231).—*Triacetyl-3:5-dibromosalicylaldehyde*,



prepared by the action of acetic anhydride on sodium 3:5-dibromosalicylaldehyde, crystallises from alcohol in colourless prisms and melts at 103° ; it is hydrolysed by boiling with dilute acids to 3:5-dibromoacetylsalicylaldehyde, $\text{OAc} \cdot \text{C}_6\text{H}_2\text{Br}_2 \cdot \text{CHO}$, which crystallises in long needles and melts at 90° . By the action of sodium acetate and acetic anhydride on 3:5-dibromosalicylaldehyde, 6:8-dibromo-

coumarin, $\text{C}_6\text{H}_2\text{Br}_2 \cdot \begin{smallmatrix} \text{CH} : \text{CH} \\ \diagdown \quad \diagup \\ \text{O} \quad \text{CO} \end{smallmatrix}$ can be directly prepared (compare Perkin, this Journal, 1871, 24, 37); the *dibromide*,

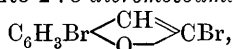


is formed very slowly by the action of bromine on dibromocoumarin dissolved in carbon disulphide, and separates in large, transparent, rhombic prisms; it crystallises from alcohol in prismatic needles and melts at 162° . Dibromocoumarilic acid, $\text{C}_6\text{H}_2\text{Br}_2 \cdot \begin{smallmatrix} \text{CH} \\ \diagdown \quad \diagup \\ \text{O} \end{smallmatrix} \cdot \text{C} \cdot \text{CO}_2\text{H}$,

prepared by hydrolysing the dibromide with alcoholic potash, melts at 276° , and is identical with that already obtained from tribromocoumarin (this vol., i, 421); the tribromocoumarin is therefore a

3 : 6 : 8-compound. *Tribromocoumarone*, $\text{C}_6\text{H}_2\text{Br}_2 \begin{smallmatrix} \text{CH} \\ \diagup \quad \diagdown \\ \text{O} \end{smallmatrix} \text{CBr}$, prepared by boiling the dibromide with sodium ethoxide for a short time, crystallises from alcohol in long, silky needles, and melts at 119° ; it is not altered by heating with alcoholic ammonia at 160° for several hours.

Perkin's α -dibromocoumarin is shown to be a 3 : 6-compound, whilst the β -dibromocoumarin is the 6 : 8-derivative. *5-Bromocoumarone*, $\text{C}_6\text{H}_3\text{Br} \begin{smallmatrix} \text{CH} \\ \diagup \quad \diagdown \\ \text{O} \end{smallmatrix} \text{CH}$, prepared by distilling bromocoumarilic acid with chalk, is a colourless oil, which solidifies in a freezing mixture and melts at 8° . The *dibromide* crystallises from absolute alcohol and melts at 95° . On boiling with sodium ethoxide for a short time, the dibromide is converted into 2 : 5-*dibromocoumarone*,



which crystallises in long needles and melts at 78.5° . T. M. L.

Tautomeric Changes in Solution. By JULIUS W. BRÜHL (*Zeit. physikal. Chem.*, 1900, 34, 31—61).—The author has studied the changes of refraction and dispersion shown by solutions of tautomeric compounds, and thus endeavoured to establish the relative stability of the enolic and ketonic forms. The molecular refraction of oxymethylenecamphor (Claisen, *Abstr.*, 1895, i, 62), determined in two such different solvents as chloroform and methyl alcohol, undergoes no change, so that the enolic form is the stable one; there is no tendency for it to pass into the ketonic form, for this transformation would betray itself in a decrease of the molecular refraction. On the other hand, the bromine derivative of oxymethylenecamphor, prepared by Aschan and Brühl (*Abstr.*, 1894, i, 613), can in the same way be shown to exist as the stable ketonic form, namely,

$$\text{C}_8\text{H}_{14} \begin{smallmatrix} \text{CBr} \cdot \text{CH} \cdot \text{O} \\ \diagup \quad \diagdown \\ \text{CO} \end{smallmatrix}.$$

A similar investigation of the α - and β -modifications of ethyl formylphenylacetate (Wislicenus, *Abstr.*, 1895, i, 366) shows that the liquid α -form is enolic, namely, $\text{OH} \cdot \text{CH} : \text{CPh} \cdot \text{CO}_2\text{Et}$; this, however, is rapidly transformed by alcoholic solvents into the ketonic form $\text{CHO} \cdot \text{CHPh} \cdot \text{CO}_2\text{Et}$. The optical behaviour of its solutions in such solvents as chloroform and benzene, which are weak in energy (compare *Abstr.*, 1899, ii, 735), shows that the solid β -modification is isomeric with the α -modification and equally saturated (possessing also an ethylene linking); it therefore differs from the ketonic form above referred to. Whether the differences between the α - and β -modifications depend on stereoisomerism, position isomerism, or unequal degree of association, cannot be determined. The alcoholic solvents, being richer in energy than chloroform or benzene, convert the solid β -ester, as quickly as the α -ester, into the liquid ketonic form.

J. C. P.

Synthesis of β -Benzoyl- α -methylpropionic (Phenylmethylbutanonoic) Acid. By TIMOTHÉE KLOBB (*Bull. Soc. Chim.*, 1900, [iii], 23, 511—512).—Pyrotartaric anhydride reacts with benzene in

the presence of aluminium chloride to form β -benzoyl- α -methylpropionic acid, $\text{CH}_2\text{Bz}\cdot\text{CHMe}\cdot\text{CO}_2\text{H}$, which crystallises in white needles melting at $135\text{--}136^\circ$, and is identical with the acid obtained by the action of potassium hydroxide on methyl phenacylmethylcyanoacetate (Abstr., 1898, i, 586). N. L.

p-Toluoyl-*o*-benzoic Acid. By HEINRICH LIMPRICHT and OTTO WIEGAND (*Annalen*, 1900, 311, 178—193. Compare Abstr., 1898, i, 322).— β -Methylantraquinone, $\text{C}_6\text{H}_4\begin{smallmatrix} \text{CO} \\ \diagup \quad \diagdown \\ \text{CO} \end{smallmatrix} \text{C}_6\text{H}_3\text{Me}$, prepared by heating a solution of *p*-toluoyl-*o*-benzoic acid in concentrated sulphuric acid, crystallises from alcohol in white needles and melts at $175\text{--}176^\circ$; the crystals are usually yellowish, however. When heated with zinc dust, the corresponding hydrocarbon, β -methylantracene, is produced; it is also formed when β -methylantraquinone is heated with zinc dust and ammonia, and crystallises from alcohol in small white scales melting at 207° .

Distillation converts *p*-toluoyl-*o*-benzoic acid into substances resulting from elimination of water. At least two compounds are produced, melting at $205\text{--}212^\circ$ and $305\text{--}310^\circ$, for which the authors suggest the formulæ $\text{C}_{30}\text{H}_{22}\text{O}_5$ and $\text{C}_{30}\text{H}_{60}\text{O}_{13}$ respectively; when these are heated with alcoholic potash, *p*-toluoyl-*o*-benzoic acid is regenerated, whilst oxidation with alkaline permanganate gives rise to benzophenonedicarboxylic acid.

The compound, $\text{C}_{60}\text{H}_{42}\text{O}_9$, prepared by heating *p*-toluoyl-*o*-benzoic acid above 260° , or the chloride at 190° , is a red powder melting at $160\text{--}165^\circ$; the compound, $\text{C}_{45}\text{H}_{30}\text{O}_6$, which is also formed, is a red powder, and melts at 155° . M. O. F.

Embelic Acid. By ARTHUR HEFFTER and W. FEUERSTEIN (*Arch. Pharm.*, 1900, 238, 15—28. Compare Warden, *Pharm. J.*, 1888, [iii], 18, 601; 19, 305).—Orange-red embelic acid, $\text{C}_{18}\text{H}_{28}\text{O}_4$, melting at 142° , was prepared by extracting with ether the powdered berries of *Ribes embelia*, Burm. (*Myrsinaceae*); no other well-characterised constituent could be isolated. The acid dissolves in alkalis, and greyish-violet alkali salts are precipitated when excess of the alkali is added; with salts of the heavy metals coloured, flocculent precipitates are obtained; the dark brown silver salt has the composition $\text{C}_{18}\text{H}_{26}\text{O}_4\text{Ag}_2$. The acid condenses with amines, 1 mol. of water being eliminated; the products are hydrolysed by dilute acids; *anilinoembelic* and *o*-toluidino-embelic acids, which are reddish-violet, melt at 185° and 130° , the red *methylaminoembelic acid* melts at 166.5° . With benzoylchloride in pyridine solution, a yellowish *dibenzoyl* derivative, $\text{C}_{32}\text{H}_{36}\text{O}_6$, melting at $97\text{--}98^\circ$, is formed. With zinc powder and hydrochloric acid, reduction to *hydroembelic acid*, $\text{C}_{18}\text{H}_{30}\text{O}_4$, takes place; this acid is colourless, melts at $116\text{--}117^\circ$, and oxidises readily to embelic acid. By permanganate in the cold embelic acid is oxidised to lauric acid, $\text{C}_{11}\text{H}_{23}\cdot\text{CO}_2\text{H}$, and formic acid; there were obtained in addition oily acids, not volatile with steam, and forming salts that, unlike those of lauric acid, are not decomposed by carbon dioxide. From these reactions, the conclusion may be drawn that embelic acid has some such constitution as

$$\text{C}_{11}\text{H}_{23}\cdot\text{C}\begin{smallmatrix} \diagup \text{CO}\cdot\text{C}(\text{OH}) \\ \diagdown \text{C}(\text{OH})\cdot\text{CO} \end{smallmatrix} \text{CMe.}$$

C. F. B.

Thermochemistry of Gallic Acid. By GUSTAVE MASSOL (*Bull. Soc. Chim.*, 1900, [iii], 23, 614—615).—The heat of dissolution of anhydrous gallic acid is -4.48 Cal. Sodium gallate crystallises from water with $3\text{H}_2\text{O}$, the hydrated salt having a heat of dissolution -8.40 Cal., that of the anhydrous salt being 1.01 . Combining these values with those obtained by Berthelot (*Abstr.*, 1885, 1177) for neutralisation of gallic acid by sodium hydroxide, $\text{C}_7\text{H}_6\text{O}_5$ (sol.) + NaOH (sol.) = $\text{C}_7\text{H}_5\text{O}_5\text{Na}$ (sol.) + H_2O (sol.) + 20.86 Cal.

W. A. D.

Thermochemistry of 2:3:4-Trihydroxybenzoic Acid. By GUSTAVE MASSOL (*Bull. Soc. Chim.*, 1900, [iii], 23, 616—617).—The heat of dissolution of anhydrous 2:3:4-trihydroxybenzoic acid is -6.3 Cal.; the heats of neutralisation of the acid by successive mols. of sodium hydroxide are 1NaOH , 13.04 Cal.; 2NaOH , 6.56 Cal.; 3NaOH , 2.18 Cal.; 4NaOH , 0.96 Cal.; 5NaOH , 0.91 Cal., the total heat of neutralisation being 23.65 Cal. Although the acid contains 3 hydroxyls, the thermal values are only well defined for two of these, as in the case of gallic acid (Berthelot, *Abstr.*, 1885, 1177).

To isolate the *sodium* salt of the acid, its solution must be evaporated in a vacuum at the ordinary temperature, owing to its proneness to oxidation; it crystallises with $3\text{H}_2\text{O}$, the heat of dissolution being -6.89 Cal., that of the anhydrous salt being -1.36 Cal. The heat of formation of the salt $\text{C}_7\text{H}_6\text{O}_5$ (sol.) + NaOH (sol.) = $\text{C}_7\text{H}_5\text{O}_5\text{Na}$ (sol.) + H_2O (sol.) + 19.62 Cal., being slightly less than that of gallic acid (preceding abstract).

W. A. D.

Synthesis of Phthalidetricarboxylic Acid and Phthalidedicarboxylic Acid: a new Passage from the Aliphatic to the Aromatic Series. By OSCAR DOEBNER (*Annalen*, 1900, 311, 132—146).—The author has shown that when an aldehyde is heated with pyruvic acid and barium hydroxide, the corresponding alkylisophthalic acid is produced (*Abstr.*, 1891, 24). On subjecting glyoxylic acid to the same treatment, however, no definite product could be obtained, but a successful result was achieved by using a solution of potassium diacetoxyacetate (compare this vol., i, 473).

Phthalidetricarboxylic acid, $\text{CO}_2\text{H} \cdot \underset{\text{CO-O}}{\text{CH}} \cdot \text{C}_6\text{H}_2(\text{CO}_2\text{H})_2$, prepared by

heating potassium diacetoxyacetate with pyruvic acid and potassium or sodium hydroxide, crystallises from water in colourless needles and melts at $270-280^\circ$, after gradually losing carbon dioxide above 200° .

Phthalidedicarboxylic acid, $\text{O} \langle \underset{\text{CO}}{\text{CH}_2} \rangle \text{C}_6\text{H}_2(\text{CO}_2\text{H})_2$, obtained on boil-

ing an aqueous solution of the foregoing substance, crystallises from water in aggregates of colourless leaflets containing $2\text{H}_2\text{O}$, and melts at 286° , the water of crystallisation being driven off at 140° ; the *barium* salt contains $4\text{H}_2\text{O}$, the *strontium* salt $8\text{H}_2\text{O}$, and the *calcium* salt $6\text{H}_2\text{O}$, the *silver* salt being anhydrous. The *diethyl* ester crystallises from dilute alcohol in long needles, and melts at 112° ; the *dianilide* forms large, colourless plates, and melts above 300° .

Toluene is obtained by heating a mixture of barium phthalidedicarboxylate with barium oxide, but the result of fusing the acid with potassium hydroxide is *methylbenzenetricarboxylic acid*, $C_6H_2Me(CO_2H)_3$, which crystallises from hot water in long needles melting at about 315° . 1:2:3:4-Benzenetetracarboxylic (prehnitic) acid is produced when phthalidedicarboxylic acid is oxidised with potassium permanganate. M. O. F.

Oxidation of Benzaldoxime. By EUGEN BANBERGER (*Ber.*, 1900, 33, 1781—1788).—Benzaldoxime, when oxidised by means of Caro's reagent, yields a mixture of benzaldehyde, benzoic acid, dibenzenylazoxime, benzamide (trace), nitrous acid, benzhydroxamic acid, and *isophenyl*-nitromethane (isolated as phenylnitromethane). The formation of the two last substances is especially noteworthy; the conversion of an oxime into a hydroxamic acid is analogous to the oxidation of an aldehyde to a carboxylic acid, whilst the transformation of benzaldoxime into *isophenyl*nitromethane, which recalls the oxidation of tertiary bases to amine oxides, resembles the formation of true nitro-compounds by the oxidation of true nitroso-derivatives.

The author explains the transformation observed by Scholl (Abstr., 1888, 443) of oximes into the corresponding pseudonitroles under the action of nitrogen tetroxide, by assuming that, in the first instance, the latter oxidises the oxime to the corresponding *isonitro*paraffin. Thus acetoxime would initially yield secondary *isonitro*propane and nitrous acid, these two substances then interacting normally to form the pseudonitrole. V. Meyer's view (Abstr., 1888, 702), based on Scholl's work, that the pseudonitroles may be regarded as the nitrites, $R_2C:N \cdot O \cdot NO_2$, of the oximes, does not therefore appear to be justified; moreover, the formation of pseudonitroles by the electrolytic oxidation of ketoximes (Schmidt, this vol., i, 332) also militates against this view.

It is stated in conclusion, without experimental data being given, that substituted benzaldoximes and also acetaldoxime yield the corresponding hydroxamic acids when treated with Caro's reagent; acetaldoxime yields in addition *isonitro*ethane. Since benzylamine yields benzaldoxime when treated with Caro's reagent (this vol., i, 281), benzhydroxamic acid and *isophenyl*nitromethane are amongst the products of the oxidation of benzylamine by this method.

W. A. D.

Oxidations in Presence of Acetic Anhydride and Sulphuric Acid. By JOHANNES THIELE and ERNST WINTER (*Annalen*, 1900, 311, 353—362).—A mixture of acetic anhydride and concentrated sulphuric acid is capable of oxidising methyl derivatives of benzene to the corresponding aldehydes, which are at once converted into the diacetyl derivatives.

p-Nitrobenzaldehyde diacetate, $NO_2 \cdot C_6H_4 \cdot CH(OAc)_2$, prepared from *p*-nitrotoluene and acetic anhydride with sulphuric, acetic, and chromic acids, crystallises from alcohol in white prisms and melts at 125° ; *o*-nitrobenzaldehyde diacetate melts at 87 — 88° .

p-Hydroxybenzaldehyde triacetate, $OAc \cdot C_6H_4 \cdot CH(OAc)_2$, obtained from

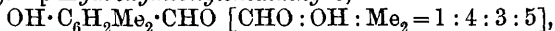
the acetyl derivative of *p*-cresol, crystallises from petroleum in prisms and melts at 93—94°.

Trihydroxybenzaldehyde pentacetate, $(\text{OAc})_3 \cdot \text{C}_6\text{H}_2 \cdot \text{CH}(\text{OAc})_2$, produced when the triacetyl derivative of trihydroxytoluene is treated in the manner described, crystallises from alcohol in white needles melting at 130°.

Terephthalaldehyde tetracetate, $\text{C}_6\text{H}_4[\text{CH}(\text{OAc})_2]_2$, prepared from *p*-xylene, crystallises from alcohol in white leaflets melting at 164°. *isoPhthalaldehyde tetracetate* melts at 101°, and *phthalaldehyde tetracetate* at 132—133°.

Phthalaldehyde, prepared by hydrolysing the tetracetate, melts at 55—56°, and the dioxime at 251°. M. O. F.

Action of Ethyl Nitrite on Trisubstituted Phenols. By JOHANNES THIELE and HEINRICH EICHWEDE (*Annalen*, 1900, **311**, 363—379).—*p*-Hydroxymesitylenealdehyde,



prepared from mesitol by the action of a concentrated solution of ethyl nitrite in alcohol, crystallises from benzene in colourless, nacreous leaflets, and melts at 113·5—114°; the *triacetate* melts at 95°, and the *benzoyl* derivative at 105°. The *phenylhydrazone* is a crystalline powder melting at 143°, and the *phenylhydrazone* of the benzoyl derivative crystallises from alcohol in colourless needles melting at 184°. The *oxime* melts at 169·5°, and yields the *hydrochloride* as a white, crystalline powder which melts and decomposes at 157°; the *diacetyl* derivative of the oxime crystallises from carbon disulphide, and melts at 113°.

p-Hydroxymesitylenonitrile, $\text{OH} \cdot \text{C}_6\text{H}_2\text{Me}_2 \cdot \text{CN}$, crystallises from petroleum in lustrous needles melting at 126°; the *acetyl* derivative, obtained when the foregoing oxime is treated with boiling acetic anhydride, forms slender, white needles melting at 98°.

p-Hydroxymesityleneimino-ether, $\text{OH} \cdot \text{C}_6\text{H}_2\text{Me}_2 \cdot \text{C}(\text{OEt}) : \text{NH}$, crystallises from benzene and melts at 144°, when it decomposes; the *hydrochloride*, obtained by passing hydrogen chloride into a boiling alcoholic solution of *p*-hydroxymesitylenonitrile, is a white powder sparingly soluble in water.

4 : 6-Dibromo-2-nitrophenol, $\text{NO}_2 \cdot \text{C}_6\text{H}_2\text{Br}_2 \cdot \text{OH}$, produced when tribromophenol is treated with a concentrated solution of ethyl nitrite in absolute alcohol, melts at 117·5°; the corresponding 4 : 6-dibromo-2-aminophenol melts at 99° (Hölz gives 91—92°).

Bromonitrocresol, $\text{NO}_2 \cdot \text{C}_6\text{H}_2\text{BrMe} \cdot \text{OH}$ [$\text{Me} : \text{NO}_2 : \text{OH} : \text{Br} = 1 : 3 : 4 : 5$], prepared from dibromo-*p*-cresol by the action of ethyl nitrite in alcohol, crystallises from alcohol in lustrous, yellow needles and melts at 69°; it is also produced by brominating *o*-nitro-*p*-cresol. *Bromoaminocresol*, $\text{NH}_2 \cdot \text{C}_6\text{H}_2\text{BrMe} \cdot \text{OH}$ [$\text{Me} : \text{NH}_2 : \text{OH} : \text{Br} = 1 : 3 : 4 : 5$], obtained by reducing the foregoing substance with stannous chloride and hydrochloric acid, crystallises from alcohol in colourless needles and melts at 93°; the *hydrochloride* forms thin, lustrous leaflets and blackens at 240—250°.

Bromonitrocresol, $\text{NO}_2 \cdot \text{C}_6\text{H}_2\text{BrMe} \cdot \text{OH}$ [$\text{Me} : \text{OH} : \text{NO}_2 : \text{Br} = 1 : 2 : 3 : 5$],
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prepared from dibromo-*o*-cresol and ethyl nitrite, melts at 88°, being identical with the substance described by Claus and Jackson.

p-Bromo- β -cresotic acid,

$\text{CO}_2\text{H} \cdot \text{C}_6\text{H}_2\text{BrMe} \cdot \text{OH}$ [Me : OH : CO_2H : Br = 1 : 2 : 3 : 5], produced on adding bromine to a solution of β -cresotic acid in glacial acetic acid, crystallises from ethyl acetate in white needles, and melts at 231—232°, when it decomposes; the *methyl* and *ethyl* esters melt at 109° and 75° respectively. The action of ethyl nitrite is very slow, the product consisting of nitrobromocresol melting at 88°.

M. O. F.

2-Methylchromone. By M. BLOCH and STANISLAUS VON KOSTANECKI (*Ber.*, 1900, 33, 1998—1999. Compare this vol., i, 308).—2-Methoxyacetylacetophenone, $\text{OMe} \cdot \text{C}_6\text{H}_4 \cdot \text{CO} \cdot \text{CH}_2\text{Ac}$, obtained when a mixture of methyl methoxysalicylate, acetone, and sodium is left for 12 hours, crystallises in long, broad, striated prisms melting at 36—37°, and in alcoholic solution gives a red coloration with ferric chloride. By the action of hydriodic acid it is converted into 2-methylchromone, $\text{C}_6\text{H}_4 \begin{smallmatrix} \text{O} - \text{CMe} \\ \diagup \quad \diagdown \\ \text{CO} \quad \text{CH} \end{smallmatrix}$, which crystallises in clusters of white needles melting at 70—71°, and, when dissolved in sulphuric acid, exhibits a violet-blue fluorescence.

R. H. P.

The Friedel-Crafts Reaction. By H. KRONBERG (*J. pr. Chem.*, 1900, [ii], 61, 494—496).—The additive compound of benzoyl chloride with aluminium chloride is regarded as having the constitution $\text{C}_6\text{H}_5 \cdot \text{CCl}_2 \cdot \text{O} \cdot \text{AlCl}_2$; this reacts with benzene to form the additive compound of benzophenone and aluminium chloride, which is formulated as $\text{CPh}_2\text{Cl} \cdot \text{O} \cdot \text{AlCl}_2$, and is decomposed by water into benzophenone and aluminium oxychloride.

T. M. L.

New Derivative of Benzophenone. By WILLIAM OECHSNER DE CONINCK and DERRIEN (*Compt. rend.*, 1900, 130, 1768—1770).—A solution of benzophenone in concentrated formic acid, when exposed to diffused light, develops a light yellow coloration which gradually deepens in tint; browner shades are produced when the solution is placed in direct sunlight. Benzophenone, which is but slightly soluble in dilute acetic acid, gradually dissolves in this medium under the influence of the solar radiation, the solution thus produced slowly developing a brown coloration.

Benzophenone, when exposed to the indigo and violet parts of the spectrum, soon melts and remains liquid, but the phenomenon is not due to allotropic change, for after solidification the substance is found to have its original melting point.

A solution of benzophenone in 95 per cent. alcohol, when exposed to direct sunlight, slowly develops a pale yellow coloration and deposits colourless, birefractive crystals melting at 182°, an appreciable quantity of aldehyde being simultaneously produced. The compound, which has the empirical formula $\text{C}_{17}\text{H}_{16}\text{O}$, is probably produced by the interaction of equal mols. of benzophenone, aldehyde, and alcohol, and may have the constitution $\text{CPh}_2\text{:CH} \cdot \text{C}(\text{Et})\text{O}$. A compound

melting at 180° is produced in a similar manner with a solution of benzophenone in methyl alcohol, whilst an alcoholic solution of acetophenone yields a substance melting at 120°. G. T. M.

Derivatives of *p*-Aminobenzophenone. By PAUL DINGLINGER (*Annalen*, 1900, 311, 147—153).—The *phenylhydrazone* of *p*-aminobenzophenone, $\text{NH}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{CPh} \cdot \text{N} \cdot \text{NHPh}$, prepared by heating an alcoholic solution of *p*-aminobenzophenone with excess of phenylhydrazine, crystallises in lustrous yellow needles and melts at 169°.

p-Benzophenylsuccinimide, $\text{COPh} \cdot \text{C}_6\text{H}_4 \cdot \text{N} \begin{smallmatrix} \text{CO} \cdot \text{CH}_2 \\ \text{CO} \cdot \text{CH}_2 \end{smallmatrix}$, obtained by fusing a mixture of succinic anhydride with *p*-benzoaniline (*p*-aminobenzophenone), crystallises from hot alcohol in small, dull-yellow prisms and melts at 175°.

Ethyl p-benzophenylloxamate, $\text{COPh} \cdot \text{C}_6\text{H}_4 \cdot \text{NH} \cdot \text{CO} \cdot \text{CO}_2\text{Et}$, produced when *p*-benzoaniline is heated with ethyl oxalate (1 mol.), crystallises from alcohol in white leaflets and melts at 112°.

p-Benzophenylmethylurethane, $\text{COPh} \cdot \text{C}_6\text{H}_4 \cdot \text{NH} \cdot \text{CO}_2\text{Me}$, obtained from *p*-benzoaniline and methyl chlorocarbonate, forms white, lustrous leaflets and melts at 155°. Fusion, followed by distillation, converts this compound into methyl alcohol and *benzophenylcarbimide*, $\text{COPh} \cdot \text{C}_6\text{H}_4 \cdot \text{N} : \text{CO}$, a yellow, granular powder which begins to melt at 201°.

Dibenzophenylcarbamide, $\text{CO}(\text{NH} \cdot \text{C}_6\text{H}_4 \cdot \text{COPh})_2$, prepared by heating benzophenylcarbimide with benzoaniline dissolved in benzene in a reflux apparatus, crystallises in small, yellow needles melting at 189°; it is more readily produced by passing phosgene into a solution of benzoaniline in boiling benzene.

p-Benzophenylthiocarbimide, $\text{COPh} \cdot \text{C}_6\text{H}_4 \cdot \text{N} : \text{CS}$, obtained by distilling dibenzophenylthiocarbamide with phosphoric acid, crystallises from benzene and melts at 122°.

p-Benzophenylthiocarbamide, $\text{COPh} \cdot \text{C}_6\text{H}_4 \cdot \text{NH} \cdot \text{CS} \cdot \text{NH}_2$, prepared by the action of ammonia on the foregoing substance, crystallises in lustrous, white leaflets and melts at 198°.

The *p*-benzoanilide of *p*-benzoanilinocinnamylformic acid, $\text{COPh} \cdot \text{C}_6\text{H}_4 \cdot \text{N} : \text{C}(\text{CH} : \text{CHPh}) \cdot \text{CO} \cdot \text{NH} \cdot \text{C}_6\text{H}_4 \cdot \text{COPh}$, produced on heating alcoholic *p*-benzoaniline with pyruvic acid and benzaldehyde, crystallises from glacial acetic acid in slender, white needles and melts at 180°.

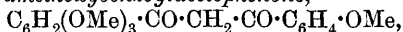
When *p*-aminobenzophenone is fused with zinc chloride, benzoic acid and benzanilide are formed. M. O. F.

Action of Ethyl Mercaptan on some Diatomic Ketones. By B. LLAGUET (*Bull. Soc. Chim.*, 1900, [iii], 23, 507—509).—Ethyl mercaptan reacts with benzoin in the presence of hydrochloric acid or zinc chloride to form a compound, $\text{CPh}(\text{SEt})_2 \cdot \text{CHPh} \cdot \text{OH}$, which crystallises from dilute alcohol in white needles melting at 93—94°, and is oxidised to benzil by potassium permanganate or nitric acid. Benzil, when similarly treated, yields a compound, $\text{CPh}(\text{SEt})_2 \cdot \text{COPh}$, which crystallises from alcohol in white, prismatic needles, and from acetic acid in octahedra melting at 73—74°; oxidation reconverts it into

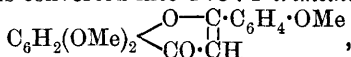
benzil. With acetyl acetone, ethyl mercaptan forms a yellow, oily liquid of the composition $\text{CMe}(\text{SEt})_2 \cdot \text{CH}_2\text{Ac}$, which has a sp. gr. 2.008 at 13.5° , and boils at $180\text{--}185^\circ$ under 240 mm. and at $179\text{--}183^\circ$ under 215 mm. pressure. When treated with sodium ethoxide in alcoholic solution, it yields a *sodium* derivative crystallising in white needles, whilst with sodium hydrogen sulphite it forms a *compound* which also crystallises in needles. No definite compounds could be isolated from its oxidation products. N. L.

Synthesis of 1:3:4'-Trihydroxyflavone (Apigenin). By J. CZAJKOWSKI, STANISLAUS VON KOSTANECKI, and JOSEF TAMBOR (*Ber.*, 1900, 33, 1988—1997).—Assuming from the researches of A. G. Perkin (*Trans.*, 1897, 71, 805) that apigenin is 1:3:4'-trihydroxyflavone, the authors have synthesised this compound, and found that pure apigenin is identical with it, but that the apigenin which Perkin used was not pure.

2:4:6:4'-Tetramethoxybenzoylacetophenone,



obtained by heating 2:4:6-trimethoxyacetophenone and ethyl anisate with sodium in xylene solution at 120° for 12 hours, crystallises in colourless plates or needles which melt at 91° . When treated with hydriodic acid, it is converted into 1:3:4'-trimethoxyflavone,



which crystallises in rosettes of long, white needles melting at 156° , and when further treated with hydriodic acid yields 1:3:4'-trihydroxyflavone, which crystallises in small, yellowish-white leaflets melting at 347° , and does not dye mordanted cotton; this proves to be identical with apigenin obtained by the purification (by means of hydriodic acid) of the crude product yielded by the hydrolysis of apiin.

1:3:4'-Triacetoxyflavone (triacetylapienin) crystallises in silky, white needles which melt at $181\text{--}182^\circ$; 3:4'-dimethoxy-1-hydroxyflavone crystallises in yellowish needles which melt at $170\text{--}171^\circ$, and yields an acetyl derivative melting at $193\text{--}194^\circ$; the corresponding diethoxy-derivatives melt at $163\text{--}164^\circ$ and $148\text{--}149.5^\circ$ respectively (compare Perkin, *loc. cit.*). R. H. P.

Oxidation of the Oximes of Unsaturated Compounds. By CARL D. HARRIES (*Ber.*, 1900, 33, 1999—2001. Compare Abstr., 1899, i, 566).— α -Mesityloxime or mesitylnitrimine, when treated with dilute nitric acid, yields a *compound*, $\text{C}_6\text{H}_9\text{O}_4\text{N}_3$, which forms golden-yellow crystals melting at $127\text{--}128^\circ$, and reacts with aniline, forming a crystalline *compound* which melts at $86\text{--}88^\circ$.

Benzylideneacetoxime, when treated with acetic acid and amyl nitrite, yields an insoluble *compound*, $\text{C}_{10}\text{H}_9\text{O}_3\text{N}_3$, which melts at 210° , and, when treated with dilute nitric acid, an easily soluble *compound* melting at 159° . R. H. P.

Action of Acetic Anhydride and Sulphuric Acid on Quinones. By JOHANNES THIELE and ERNST WINTER (*Annalen*, 1900, 311, 341—352. Compare Abstr., 1898, i, 469).—The *diacetyl*

derivative of chloroquinol, $C_{10}H_9O_4Cl$, obtained from quinone by the action of zinc chloride dissolved in acetic anhydride, crystallises from methyl alcohol in rhombic plates, and melts at $71-72^\circ$.

The *triacetyl* derivatives of 1:2:4-trihydroxynaphthalene, prepared alike from α - and β -naphthaquinones by the action of acetic anhydride mixed with concentrated sulphuric acid or zinc chloride, crystallises from alcohol in groups of needles, and melts at $134-135^\circ$; alcoholic hydrochloric acid hydrolyses it to 1:2:4-trihydroxynaphthalene, which crystallises from a large quantity of benzene in almost colourless needles melting at 154° . Alcoholic solutions of trihydroxynaphthalene darken on exposure to air, and after a long interval deposit deep red crystals of hydroxynaphthaquinone, which melt at $186-188^\circ$ and decompose at 190° ; the *acetyl* derivative, obtained by treatment with boiling acetic anhydride, and also by the action of acetic anhydride mixed with concentrated sulphuric acid, crystallises from alcohol in yellow leaflets and melts at 130° .

The diacetyl derivative of naphthazarine (dihydroxy- β -naphthaquinone) is readily obtained by treating naphthazarine with a solution of zinc chloride in acetic anhydride, or a mixture of the latter substance with concentrated sulphuric acid. The *pentacetyl* derivative of pentahydroxynaphthalene, $C_{20}H_{18}O_{10}$, produced by the further action of acetic anhydride mixed with concentrated sulphuric acid, separates from alcohol as a white, crystalline powder melting at 179° .

Trihydroxynaphthaquinone, $C_{10}H_6O_5$, prepared by hydrolysing the foregoing pentacetyl derivative with alcoholic sulphuric acid, rendering the dark liquid faintly alkaline with sodium carbonate, and then acidifying with sulphuric acid, separates from xylene as a red, crystalline powder which melts at 195° .

The *triacetyl* derivative of trihydroxytoluene, prepared by the action of acetic anhydride mixed with concentrated sulphuric acid on toluquinone, crystallises from alcohol and melts at $114-115^\circ$; hydrolysis converts it into 2:4:5-trihydroxytoluene, which melts at $131-132^\circ$.

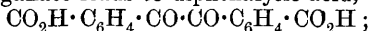
p-Hydroxytoluquinone, $C_7H_6O_3$, produced on oxidising trihydroxytoluene with ferric chloride, crystallises from xylene in lustrous, yellow leaflets which melt and decompose at 142° ; the *acetyl* derivative separates from petroleum in slender, yellow prisms and melts at $75-76^\circ$.

The *tetracetyl* derivative of tetrahydroxytoluene, prepared by the action of acetic anhydride mixed with concentrated sulphuric acid on hydroxytoluquinone, separates from methyl alcohol as a white, crystalline powder melting at $132-133^\circ$; *tetrahydroxytoluene* $[Me:(OH)_4 = 1:2:3:4:5 \text{ or } 1:2:4:5:6]$ separates as a crystalline powder from toluene and melts at $170-171^\circ$.
M. O. F.

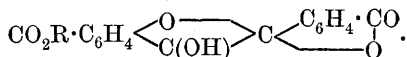
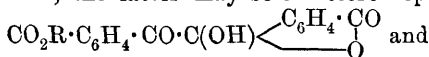
Oxidation Products of Chrysene. By CARL GRAEBE and F. HÖNIGSBERGER (*Annalen*, 1900, 311, 257-275. Compare Abstr., 1896, i, 443).—Chrysoquinone was first obtained by Liebermann on oxidising the hydrocarbon with chromic acid in acetic acid, but it is found more convenient to substitute sodium dichromate for chromic acid as only one-fourth the quantity of acetic acid is then required. The quinone melts at 235° (239.5° corr.). When the blue solution

in concentrated sulphuric acid is largely diluted, the liquid exhibits a characteristic absorption spectrum having a broad, dark band, λ 610—540; concentrated solutions cut off the orange, the yellow, and a portion of the green of the spectrum.

Further oxidation of chrysoquinone with a boiling dilute solution of potassium permanganate leads to diphthalic acid,



the *calcium* salt contains $\frac{1}{2}\text{H}_2\text{O}$, which is removed at 150° , and the *potassium* salt is anhydrous. Both salts are yellow, and the dimethyl ester is yellow, the monomethyl and monoethyl esters being colourless; the latter may be therefore represented by one of the formulæ



Diphthalic acid, unlike benzilmonocarboxylic acid, occurs in one modification only, and this is colourless; it is best represented, therefore,

by the tautomeric formula $\text{C}_6\text{H}_4 \begin{array}{c} \text{C}(\text{OH}) \cdot \text{C}(\text{OH}) \\ \diagup \quad \diagdown \\ \text{CO} \cdot \text{O} \end{array} \text{C}_6\text{H}_4$, support

being given to this expression by the fact that acetyl chloride converts the substance into the *diacetyl* derivative, which crystallises from glacial acetic acid in colourless needles and melts at 234° . Diphthalic acid is also produced by the oxidation of chrysoketone with potassium permanganate.

Chrysenic acid, $\text{C}_{10}\text{H}_7 \cdot \text{C}_6\text{H}_4 \cdot \text{CO}_2\text{H}$, obtained by Bamberger and Burgdorf from the action of fused caustic potash on chrysoquinone and chrysoketone, is more conveniently prepared by adding a mixture of chrysoquinone and lead peroxide to the fused alkali; it melts at 187 — 189° (190° corr.). The *amide* melts at 169.5° .

2'-Amino-2-phenylnaphthalene, $\text{C}_{10}\text{H}_7 \cdot \text{C}_6\text{H}_4 \cdot \text{NH}_2$, prepared by the action of sodium hypobromite on the amide of chrysenic acid, crystallises from dilute alcohol in needles and melts at 95° ; the *hydrochloride* melts at 205° .

Chrysoquinoneoxime, $\text{C}_{16}\text{H}_{10} \begin{array}{c} \text{C:NOH} \\ \diagup \quad \diagdown \\ \text{CO} \end{array}$, obtained by heating the

quinone with alcoholic hydroxylamine (1 mol.), crystallises from glacial acetic acid and melts at 160 — 161° ; the solution in concentrated sulphuric acid is reddish-violet, and boiling dilute caustic soda dissolves it also, forming a yellowish-brown liquid, which, on cooling, deposits bronze-coloured needles of the *sodium* derivative.

According to the conditions under which the change is effected, the Beckmann transformation of chrysoquinoneoxime gives rise to two amic acids. The action of glacial acetic acid, saturated with hydrogen chloride, converts chrysoquinoneoxime at 100° into the *amic acid*, $\text{C}_{18}\text{H}_{18}\text{O}_3\text{N}$, which melts at 220° , and the *isomeride* melting at 260° , of which the former preponderates; if the transformation is carried out at 130 — 140° , the latter substance is produced, along with *chrysoketone-carboxylic acid*, $\text{C}_{10}\text{H}_5(\text{CO}_2\text{H}) \begin{array}{c} \text{C} \\ \diagup \quad \diagdown \\ \text{CO} \end{array}$ or $\text{C}_{10}\text{H}_6 \begin{array}{c} \text{C} \\ \diagup \quad \diagdown \\ \text{CO} \end{array}$, which melts at 283° , and yields chrysoketone when distilled with lime. M. O. F.

Influence of the Amount of Water on the Specific Rotation of Alcoholic Solutions of Camphor. Valuation of Spirit of Camphor. By ALFRED PARTHEIL and A. VAN HAAREN (*Arch. Pharm.*, 1900, 238, 164—166).—It is shown that the percentage of camphor dissolved in aqueous alcohol is very approximately given by $1.5152a$, where a is the rotation produced in a 200 mm. tube; the sp. gr. of the alcohol used has little influence on the result. For finding the sp. gr. of the alcohol used in preparing a sample of spirit of camphor, the expression $100 - p \frac{100}{d} - 1.05 p$ gives good results, p denoting the percentage of camphor present, and d the sp. gr. of the camphor spirit.
W. A. D.

Decomposition Products of Campherimine. By FRIEDRICH MAHLA and FERDINAND TIEMANN (*Ber.*, 1900, 33, 1929—1939. Compare Abstr., 1896, i, 85).—When campherimine is heated on the water-bath in a reflux apparatus attached to wash-bottles containing alcohol, and air is slowly bubbled through the hot liquid for 8—10 hours, the products are camphor, dihydrocamphenonitrile, the corresponding amide, and the nitrile of *isopropylheptanonic acid*.

Dihydrocamphenonitrile, $\text{CN} \cdot \text{CH}_2 \cdot \text{CH} \begin{smallmatrix} \text{CMe}_2 \cdot \text{CHMe} \\ | \\ \text{CH}_2 - \text{CH}_2 \end{smallmatrix}$, is readily volatile in steam and forms a colourless liquid boiling at 225—228°; it has a sp. gr. 0.90904, refractive index 1.46108, molecular refraction 45.60, and its rotation in a 10 cm. tube is +28°53'. The corresponding *amide*, readily obtained by the partial hydrolysis of the nitrile with alcoholic potassium hydroxide, crystallises from ethyl acetate in plates melting at 143° and is readily soluble in most organic solvents with the exception of light petroleum; it is dextrorotatory and when boiled for some time with alcoholic potash yields *dihydrocamphenonic acid*, $\text{C}_{10}\text{H}_{18}\text{O}_2$, which is best purified by passing ammonia into the dry ethereal solution of the acid and decomposing the ammonium salt with mineral acid. It is a colourless oil, distils at 160° under 22 mm. or at 258° under atmospheric pressure, has a sp. gr. 0.98048, refractive index 1.46277, molecular refraction 47.73, and its rotation in a 10 cm. tube is +28°26'. It is readily volatile in steam, yields insoluble *calcium*, *silver*, *lead*, and *copper* salts, and does not combine with bromine, but readily decolorises dilute alkaline permanganate. Its *ethyl* ester distils at 230° and in a 10 cm. tube has a rotation +25°33'. The acid is probably identical with that described by Guerbet (*Abstr.*, 1895, i, 61). When oxidised with alkaline permanganate, it yields an *acid*, $\text{CO}_2\text{H} \cdot \text{CH}_2 \cdot \text{CH} \begin{smallmatrix} \text{CH}_2 - \text{CH}_2 \\ | \\ \text{CMe}_2 \cdot \text{C}(\text{OH}) \cdot \text{CO}_2\text{H} \end{smallmatrix}$, crystallising in rhombic plates melting at 175°, together with a small amount of an *acid*, $\text{C}_{10}\text{H}_{14}\text{O}_6$, which crystallises in rhombic prisms melting at 198°, and readily soluble in ether, alcohol, or water; the latter is also obtained when the hydroxy-acid, $\text{C}_{10}\text{H}_{16}\text{O}_5$, is further oxidised with permanganate, but if Beckmann's mixture is employed, *isocamphoronic acid* is formed; *isocamphoronic acid* is also obtained when hydrocamphenonic acid is oxidised with nitric acid.

5-isopropylheptanone-2-nitrile-7, $\text{CN} \cdot \text{CH}_2 \cdot \text{CHPr}^{\beta} \cdot \text{CH}_2 \cdot \text{CH}_2\text{Ac}$, ob-

tained by fractional distillation under reduced pressure from the products which are not volatile in steam, is an oil distilling at 174—180° under 32 mm. pressure or, after purification, by aid of its *semicarbazone* (which melts at 135°), at 157° under 16 mm. pressure. It has a sp. gr. 0.9402 at 23°, a refractive index 1.45129, and a molecular refraction 47.83. When boiled with alcoholic potash for 3 hours, the greater part of the nitrile is transformed into an isomeric substance, $C_{10}H_7ON$, melting at 127°; this yields a *semicarbazone* melting at 214°, has feebly basic properties, and yields a sparingly soluble *aurichloride*; when warmed with excess of mineral acids, an odour of carvone is developed, and an oil formed which yields a *semicarbazone* melting at 154°.

*iso*Propylglutaric acid is formed when the *isopropylheptanononitrile* is oxidised with permanganate. J. J. S.

Citral and its Isomeric Forms. By PHILIPPE BARBIER (*Bull. Soc. Chim.*, 1900, [iii], 23, 617—618).—A claim for priority.

W. A. D.

Syntheses in the Terpene Series. By IWAN L. KONDAKOFF and IWAN SCHINDELMEISER (*J. pr. Chem.*, 1900, [ii], 61, 477—490).—Tables are given of the values recorded by previous workers and those obtained in the present research for the physical constants of 1-methyl-3-cyclohexanone, 1-methyl-3-cyclohexanol, 1-methyl-3-cyclohexanol bromide, and tetrahydrotoluene. In presence of zinc chloride, tetrahydrotoluene forms with acetyl chloride an additive compound which has an odour similar to that of carvone, and yields an oxime; with moist silver oxide, it is converted into a keto-alcohol. Additive compounds with acetic anhydride and acetic acid are also formed under similar conditions.

In the reduction of 1-methyl-3-cyclohexanone, a crystalline substance is produced which is not volatile with steam; when crystallised from water, it forms hydrated crystals melting at 73°, but when dried in a desiccator melts at 93—94°, or at 92.5° when crystallised from alcohol; a 10 per cent. solution has $\alpha + 1.01'$ in a 1 dcm. tube at 20°; the substance appears to give two bromides, one liquid and the other a solid melting at 126°; on treating the bromide with moist silver oxide, the product has a powerful odour of pelargonium oil. The substance is probably a pinacone, as has been suggested by Wallach (*Nachrichten K. Ges. Wiss. Göttingen*, 1897, 315). T. M. L.

Action of Fuming Nitric Acid on Camphene. By LOUIS BOUVEAULT (*Bull. Soc. Chim.*, 1900, [iii], 23, 535—540).—When camphene is dissolved in chloroform and gradually added to well-cooled fuming nitric acid, it is converted into a mixture of two isomeric nitrates of the composition $C_{10}H_{16}.HNO_3$, one of these being decomposed when distilled under diminished pressure, whilst the second is more stable, boils at 110° under 10 mm. pressure, has a sp. gr. 1.0988 at 0°, and is converted by treatment with alcoholic potash into camphene and potassium nitrate. Since the nitrates of secondary alcohols are very frequently converted by the action of potash into potassium *nitrite* and a ketone, it seems probable that the nitrate described is derived from a tertiary alcohol, and that camphene itself

has not the constitution $C_8H_{14} \begin{smallmatrix} <CH \\ | \\ CH \end{smallmatrix}$, but contains the complex $>C:CH_2$ or $\geq C \cdot CH_3$. This result is shown to be in accordance with the author's views on the constitution of camphor and its derivatives. N. L.

Isoprene. By WLADIMIR MOKIEWSKY (*J. Russ. Phys. Chem. Soc.*, 1900, 32, 207—216. Compare Abstr., 1899, i, 726).—On oxidising isoprene dibromide with permanganate, the corresponding glycol (dibromohydrin) is obtained, and this by the action of zinc dust is converted into a hydrocarbon (*loc. cit.*), which the author now shows to be identical with isoprene. If isoprene has the open-chain formula, $CH_2:CM e \cdot CH:CH_2$, the hydrocarbon obtained by the reduction of the dibromohydrin would have the structure $CM e \begin{smallmatrix} <CH_2 \\ | \\ CH \end{smallmatrix} > CH_2$, whilst if the latter be taken as the formula of isoprene, its dibromohydrin should yield the open-chain compound $CH_2:CM e \cdot CH:CH_2$, the identity of the initial and end products being in either case due to isomeric change. By the action of an acetic acid solution of hydrogen bromide on isoprene, a bromide is obtained of the composition C_5H_9Br ; it boils at 66—67°, and has the sp. gr. 1·3075 at 0°/0° and 1·2819 at 20°/0°; the same bromide is obtained from *as*-dimethylallene and hydrogen bromide. On treating this bromide with alcoholic potash, the corresponding alcohol, $C_5H_{10}O$, prepared by Kondakoff (*J. Russ. Phys. Chem. Soc.*, 1889, 61) is obtained; it boils at 97—99°, and has the sp. gr. 0·8417 at 0°/0° and 0·8242 at 20°/0°. [With NICOLAI A. MENSCHUTKIN.—The constant of esterification of this alcohol at 100° by acetic anhydride in presence of 15 volumes of benzene is 0·00025, the corresponding values for allyl and α -methylallyl alcohols, methylallylcarbinol, and trimethylcarbinol being 0·02871, 0·02673, 0·00643, and 0·00091 respectively.] These numbers show that the alcohol from isoprene is tertiary, as also is the bromide from which it is prepared; and the open-chain formula for isoprene is the only one which can give rise to a tertiary bromide identical with that obtained from *as*-dimethylallene.

The statement of Ipatieff (Abstr., 1899, i, 657) that a primary bromide is obtained by the addition of hydrogen bromide to diethylallene is regarded by the author as erroneous. T. H. P.

Civet, Jasmine, and Oil of Roses. By HEINRICH WALBAUM (*Ber.*, 1900, 33, 1903—1905).—Commercial civet, prepared from the African civet-cat, *Viverra civetta*, has a strongly faecal odour, and contains 0·1 per cent. of scatole, but no indole. As oil of jasmine, obtained from the pomade prepared by means of civet, contains indole (Hesse, Abstr., 1899, i, 48), although the oil extracted from the fresh jasmine blossoms does not contain this (Hesse, this vol., i, 454), it appears that the indole is developed in the blossoms after being plucked and during their treatment with the civet. Similarly, rose blossoms on keeping appear to elaborate phenylethyl alcohol, since the latter is present in marked quantity in the oil obtained from

dried rose leaves, although it is entirely absent from oil of roses prepared from fresh blossoms. W. A. D.

Essential Oil of Jasmine. By PAUL JEANCARD and SATIE (*Bull. Soc. Chim.*, 1900, [iii], 23, 555—556).—The discrepancies between the results obtained by Verley (*Abstr.*, 1899, i, 376) and by Hesse and Müller (*Abstr.*, 1899, i, 377, 441) in the examination of essential oil of jasmine are attributed to the fact that the oil was extracted from jasmine pomade, in the preparation of which rose-water, oil of orange flowers, benzoin, and alum are sometimes used. The following results were obtained from samples of oil of jasmine prepared (1 and 2) from pomade without extraneous additions; (3) by direct distillation from the flowers; (4) by distillation of flowers from which a portion of the odoriferous substances had been previously extracted by the usual process (*enfleurage à froid*).

	1.	2.	3.	4.
Sp. gr. at 17.5°.....	0.9099	0.9201	0.9246	0.8900
Rotatory power per 100 mm.	+ 2°30'	+ 2°40'	+ 1°40'	+ 3°50'
Saponification number	103.6	126.0	155	77
Esters as linalyl acetate, per cent. ...	36.26	44.10	54.39	26.95
Esters as benzyl acetate, per cent. ...	27.70	33.75	41.65	20.62
				N. L.

Empyreumatic Oil of Juniper. By CATHELINEAU and JEAN HAUSER (*Bull. Soc. Chim.*, 1900, [iii], 23, 557—559. Compare *Abstr.*, 1899, i, 536, 711).—The dark brown resin, soluble in caustic soda, of which 19 grams were obtained, as previously described (*Abstr.*, 1899, i, 536), from 400 c.c. of empyreumatic oil of juniper, is separated by treatment with ether into a semi-liquid portion, of agreeable odour, which could not be identified, and an insoluble substance having the composition $C_{12}H_{11}O_3$, or some multiple of this. The latter, which has the properties of a feeble acid, is precipitated by acids from its solution in alkalis in the form of brown, amorphous flocks, but when the liquid is shaken with ether and warmed, these are converted into microscopic crystals. The acid is insoluble in water or ether, but more or less soluble in alcohol, chloroform, or concentrated acetic acid.

N. L.

Essential Oil of Lavender and the Causes of the Variation in the amount of Esters contained in it. By PAUL JEANCARD and SATIE (*Bull. Soc. Chim.*, 1900, [iii], 23, 549—554).—A number of samples of oil of lavender from various sources were examined in order to ascertain the conditions influencing the proportion of esters, by which the commercial value of the oil is determined. The altitude of the place of growth appears not to affect the chemical composition and physical properties of the oil, although it may possibly have some influence on the delicacy of the perfume. The oil obtained from the flowers is incomparably superior in odour to that from the leaves and stalks, but no great differences in the chemical and physical characters

of the two are found. The conduct of the distillation is the most important factor in the production of an oil rich in esters. This operation should be carried out as quickly as possible, in order to avoid loss by partial hydrolysis, whilst at the same time it should be pushed to its utmost limit, since the proportion of esters in the various fractions increases continuously as the distillation progresses. The water used should contain but little dissolved solids. N. L.

Essential Oils of Neroli and Petit Grain. By PAUL JEANCARD and SATIE (*Bull. Soc. Chim.*, 1900, [iii], 23, 605—608).—Charabot and Pillet's (Abstr., 1899, i, 620) analyses, indicating the presence in oil of neroli of 10—20 per cent., and in oil of petit grain of 50—70 per cent., of esters calculated as linalyl acetate, are confirmed by the examination of a number of oils distilled in May, 1899. The yield of oil of neroli increased towards the end of the month, the weather being fine, but was diminished in wet weather; this variation is the reverse of that observed with oil of rose, larger yields of which are obtained in wet weather. The proportion of esters appears to be independent of the origin of the flowers. Some experiments are described which show that 5—6 per cent. of the esters contained in oil of neroli are hydrolysed when the oil is prepared by distillation. N. L.

Preparation of Gentiopicroin, the Glucoside of Fresh Gentian Root. By ÉMILE BOURQUELOT and HENRI HÉRISSEY (*Compt. rend.*, 1900, 131, 113—115).—The fresh gentian root is cut into small pieces and quickly dropped into boiling alcohol in order to destroy the oxidising and hydrolytic ferments which would otherwise lead to loss of the glucoside. The liquid is boiled for 30 mins. in a reflux apparatus, cooled, filtered, the alcohol removed by evaporation, and the residual liquid mixed with chalk, again filtered, evaporated to a syrup, and left to crystallise for a fortnight. The mass of needles thus obtained is recrystallised from a mixture of equal volumes of chloroform and 95 per cent. alcohol. The rotatory power of gentiopicroin in 2 per cent. aqueous solution was found to be $[\alpha]_D - 196^\circ$. N. L.

Glucosides Containing Thiocarbimides. By H. TER MEULEN (*Rec. Trav. Chim.*, 1900, 19, 37—45).—By distilling large quantities of *Tropaeolum majus* in steam, Hofmann obtained benzyl cyanide (Abstr., 1874, 792). Gadamer (Abstr., 1899, i, 930, and this vol., i, 49), working on a large scale, noticed the production of both benzyl cyanide and benzyl thiocarbimide, whilst smaller quantities of the plant yielded only the latter compound.

The author is of opinion that the cyanide is not present in the glucoside, but that it is produced by the prolonged action of boiling water on the thiocarbimide. The thiocarbimides have a characteristic toxic action on *Saccharomyces mycoderma*, whereas this organism is not affected by benzyl cyanide, cyanates, or organic sulphides. This reaction may be employed in detecting a thiocarbimide, and also in estimating the amount of this substance present in a solution. On adding to a culture of *S. mycoderma* in beer a solution of benzyl-

thiocarbimide which has been previously heated at 100° for 4 hours, it is found that the diminution of physiological activity corresponds with the decomposition of 90 per cent. of the thiocarbimide. The glucoside of *T. majus* has no physiological activity, the toxic action being only manifested after its hydrolysis either by the enzyme of the plant or by myrosin. Diastase and emulsin do not decompose this glucoside.

The leaves of *Cochlearia officinalis* and *Cardamine pratensis*, the roots of *Reseda odorata*, *Cochlearia armoracia*, and *Isatis tinctoria*, and the seeds of the black and white radish and several varieties of *Brassica* contain thiocarbimides in the form of glucosides, accompanied by enzymes apparently identical with myrosin. G. T. M.

Aloins. By EUGÈNE LÉGER (*Compt. rend.*, 1900, 131, 55—58).—After seven crystallisations from methyl alcohol, barbaloin no longer gives Klunge's reaction with copper sulphate and sodium chloride, although the development of a red coloration was formerly considered to be a distinctive test for this aloin. On the other hand, *isobarbaloin* readily develops a violet-red coloration, and the reaction may be employed in removing the last traces of this substance from barbaloin.

A hot aqueous solution of barbaloin containing a small amount of *isobarbaloin* is treated with excess of copper sulphate and sodium chloride until the crystals which separate on cooling no longer give the colour reaction; the product consisting of pure barbaloin is then recrystallised from methyl alcohol.

The triacetyl derivative of pure trichlorobarbaloin melts at 164·8°, whereas specimens contaminated with the corresponding derivative of *isobarbaloin* melt at 152—153°.

Tribromobarbaloin, $C_{16}H_{13}Br_3O_7 \cdot 3H_2O$, formed by the action of bromine water on pure barbaloin, crystallises from dilute alcohol in yellow needles; it differs in appearance, solubility, and water of crystallisation from the ordinary so-called "tribromobarbaloin," which in reality is tribromo*isobarbaloin*.

The least soluble constituent of the aloins from Cape aloes is identical in every respect with pure barbaloin. G. T. M.

Nature of Klunge's Aloin Reaction and the Oxidising Action of Cupric Salts in Presence of Cyanogen Compounds. By EDUARD SCHAER (*Arch. Pharm.*, 1900, 238, 279—298).—The violet-red coloration exhibited by solutions of aloes in presence of copper sulphate and hydrocyanic acid is also developed by other cupric salts, including the oxide, and by the thiocyanates, ferrocyanides, alkyl cyanides, natural and synthetical alkylthiocarbimides, and haloid salts; the colour-tone is purest when a very dilute solution of the copper salt is used. On only one occasion did the 'aloin-red' separate in a solid form as an amorphous, carmine-red precipitate; it is only very slightly soluble in water and in most organic solvents, but dissolves in alcohol, aqueous ammonia, and quite readily in a strong solution of chloral hydrate; in the pure state, it is fairly stable, although the crude solution very rapidly decomposes.

'Aloin-red' appears to be produced as one stage in the spontaneous oxidation of aloin solutions in air at the ordinary temperature or on a water-bath, but the colour is not developed by air that has been

ozonised with moist phosphorus, or in presence of bitter almond oil; metallic and colloidal mercury and colloidal platinum cause a rapid development of the red coloration, and iodine, unlike chlorine and bromine, has a similar action; nitrous acid, permanganate, ferrocyanide, and nitroprusside give 'aloin-red,' but chromic acid and hypochlorites are indifferent; silver nitrate acts gradually, but mercuric nitrate not at all; the higher oxides of manganese, nickel, and cobalt give the red coloration.

'Aloin-red' is reduced by a large number of agents, including some peroxides. When its solutions are kept, a sediment gradually deposits which, when crystallised from toluene, is obtained in minute, orange-yellow needles, and shows the reactions of alochryesine.

T. M. L.

Colouring Matter of Annatto. By KARL G. ZWICK (*Arch. Pharm.*, 1900, 238, 58—80. Compare Etti, *Abstr.*, 1878, 739).—No colouring matter ("orellin") is to be found in annatto. The bixin could not be obtained crystalline by Etti's method; a surer means (*Abstr.*, 1897, i, 630) is repeated extraction, alternately with chloroform and light petroleum, in the former of which it is soluble, whilst insoluble in the latter. It melts at 189° to a reddish liquid. Its formula, $C_{28}H_{34}O_5$, can perhaps be resolved into $OMe \cdot C_{27}H_{29}(\cdot O)_2(OH)_2$, for it contains one methoxyl group, and yields a diphenylhydrazone and a dipotassium salt; it could not, however, be made to form an acetate or benzoate. No conclusive result could be obtained by reduction with sodium in moist ether, or by distillation with zinc dust in a current of hydrogen gas, or by zinc and acetic acid; by oxidation with potassium permanganate, or potassium dichromate and acetic acid, or nitric acid (in which case a nitro-compound appears to be formed, and not oxalic acid); by fusion with potassium hydroxide or by distillation with lime. On the other hand, palmitic acid was obtained by distilling either bixin or annatto itself with superheated steam. C. F. B.

Alkaloids Present in the Seeds of Anagyris Fœtida. By ERNST SCHMIDT (*Arch. Pharm.*, 1900, 238, 184—191).—An introductory survey of the facts recorded in the two following abstracts. A report by Hans Meyer as to the physiological activity of anagyrine hydrobromide is appended showing that the latter is very different in its action from cytisine, for whilst cytisine, like strychnine, produces convulsions, anagyrine has little more effect on a dog than to enhance reflex excitability.

W. A. D.

Anagyrine. By F. M. LITTERSCHEID (*Arch. Pharm.*, 1900, 238, 191—227. Compare Klostermann, *Abstr.*, 1899, i, 959, and following abstract).—Anagyrine, prepared by Partheil and Spasski's method (*Apoth. Zeit.*, 1895, 10, 903) from the seeds of *Anagyris fœtida*, is always contaminated by more or less cytisine; the pure alkaloid is best obtained by adding an excess of phenylthiocarbimide to an alcoholic solution of the crude substance, and, after three days, collecting the precipitate of the insoluble cytisine phenylthiocarbimide thus formed (this vol., i, 516). The filtrate, on evaporation to a syrupy consistence, yields on extracting with dilute hydrochloric acid

a solution from which pure anagyrene can be obtained by adding alkali and extracting the liberated base with chloroform. A careful examination of the seeds of *Anagyris foetida* shows that they contain no other alkaloid beside cytisine and anagyrene, the ratio in which these substances occurs varying from 3 : 1 to 3 : 2.

The early part of the paper confirms most of the statements made by Klostermann (*loc. cit.*) with regard to anagyrene; the following facts are, however, new. Anagyrene mercurichloride crystallises from water containing hydrochloric acid and mercuric chloride in three forms: (1), with $\frac{1}{2}\text{H}_2\text{O}$; aggregates of large, transparent, colourless prisms, melting at $225\text{--}226^\circ$; (2), sheaves of anhydrous, slender, white needles, melting indefinitely at $213\text{--}214^\circ$; (3), white, nodular crystals melting at 231° (compare Klostermann). *Anagyrene hydriodide*, $\text{C}_{15}\text{H}_{22}\text{ON}_2\cdot\text{HI}\cdot\text{H}_2\text{O}$, crystallises from alcohol in stellar aggregates of yellow needles, and does not melt at 250° ; of the *periodides*, (1), $\text{C}_{15}\text{H}_{22}\text{ON}_2\cdot\text{HI}\cdot\text{I}$, forms beautiful, lustrous, brownish-red needles; (2), $\text{C}_{15}\text{H}_{22}\text{ON}_2\cdot\text{HI}\cdot\text{I}_2$, forms steel-grey, lustrous needles or plates, and is unstable, evolving iodine.

Anagyrene methochloride aurichloride, $\text{C}_{15}\text{H}_{22}\text{ON}_2\cdot\text{MeCl}\cdot\text{AuCl}_3$, prepared by adding auric chloride to the solution obtained on decomposing anagyrene methiodide with silver chloride, melts at $198\text{--}199^\circ$; the *platinichloride*, $\text{C}_{15}\text{H}_{22}\text{ON}_2\cdot\text{MeHPtCl}_6\cdot\text{H}_2\text{O}$, forms small, yellowish-red needles. *Anagyrene ethiodide*, $\text{C}_{15}\text{H}_{22}\text{ON}_2\cdot\text{EtI}\cdot\text{H}_2\text{O}$, forms brittle, yellow needles; the salt, $\text{C}_{15}\text{H}_{22}\text{ON}_2\cdot\text{EtCl}\cdot\text{AuCl}_3$, is amorphous.

Boiling acetic anhydride in presence of anhydrous sodium acetate is without action on either anagyrene or cytisine, showing that in neither alkaloid is a hydroxyl group present.

Anagyrene on treatment with cold 10 per cent. aqueous barium permanganate yields an *oxide*, $\text{C}_{15}\text{H}_{20}\text{O}_2\text{N}_2$, by loss of 1 mol. of hydrogen and the addition of 1 atom of oxygen; it crystallises from chloroform, on adding light petroleum, in large, silky needles, or stellar aggregates of smaller needles, melts at 195° , and is laevorotatory both in aqueous and in hydrochloric acid solution. It reddens blue litmus although, as a base, it yields an *aurichloride*, $\text{C}_{15}\text{H}_{20}\text{O}_2\text{N}_2\cdot\text{HAuCl}_4$, which crystallises from alcohol in dark golden-yellow, transparent, rhombic prisms, and melts at 225° ; the *platinichloride*, $\text{C}_{15}\text{H}_{20}\text{O}_2\text{N}_2\cdot\text{H}_2\text{PtCl}_6\cdot 2\text{H}_2\text{O}$, crystallises from water in stellar aggregates of needles and melts and decomposes at 240° ; the *mercurichloride*, $\text{C}_{15}\text{H}_{20}\text{O}_2\text{N}_2\cdot\text{HCl}\cdot\text{HgCl}_2$, forms monoclinic (?), lustrous, colourless prisms, and melts at $226\text{--}227^\circ$.

Acetic anhydride and benzoic anhydride are without action on anagyrene oxide, and the same is true of hydroxylamine; the oxide thus contains neither hydroxylic nor carbonylic oxygen. Since, also, it fails to interact with zinc and hydrochloric acid, or with sulphurous acid, it does not appear to contain its added oxygen combined with quinquevalent nitrogen as in the oxides of tertiary aromatic bases (Merlin, *Abstr.*, 1893, i, 113; Wernick and Wolfenstein, *Abstr.*, 1898, i, 536).* It is a tertiary base since it is not acted on by nitrous acid, but further research will be necessary to establish its nature.

* Compare also Bamberger and Tschirner, *Abstr.*, 1899, i, 347, 682.—W. A. D.

Since a comparison of anagryne and cytosine appears to indicate that the former is a butylcytosine, the action on cytosine of *n*-, *iso*-, *sec*-, and *tert*-butyl iodides, both alone and in presence of the corresponding alcohol, at temperatures of 100° and 150°, was studied, but in nearly all cases no action occurred; *isobutyl* bromide and *tert*-butyl chloride also gave negative results. On heating *isobutyl* iodide and cytosine, however, with alcoholic potassium hydroxide for 3 hours at 100°, *isobutylcytosine* appears to be formed in small quantity; it was isolated as the *platinichloride*, $C_4H_9 \cdot C_{11}H_{18}ON_2 \cdot H_2PtCl_6 \cdot 1\frac{1}{2}H_2O$, in the form of dark red, transparent needles, darkening at 230°, and decomposing at about 250°. A *sec-butylcytosine platinichloride* crystallising with $3H_2O$ in reddish-yellow crystals, and with $1\frac{1}{2}H_2O$ in four-sided plates, was also obtained; but in this case, as with the *isobutyl* compound, insufficient salt was isolated to enable a definite comparison with anagryne platinichloride to be made.

The action of *sec*-butyl iodide on methylcytosine under different conditions was also studied, but in every case a negative result was obtained.

W. A. D.

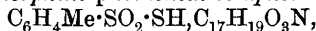
Anagryne. By MAX KLOSTERMANN (*Arch. Pharm.*, 1900, 238, 227—230).—The facts dealt with in this paper have already appeared (*Abstr.*, 1899, i, 959).

W. A. D.

Arginine. By ERNST SCHULZE (*Zeit. physiol. Chem.*, 1900, 29, 329—333).—Gulewitsch is of opinion that the arginine he has prepared from animal sources is different from 'vegetable arginine.' The present paper shows that this is not the case; the differences noted are all explicable on other grounds.

W. D. H.

Alkylthiosulphonates of Organic Bases. By JULIUS TROEGER and OTTO LINDE (*Arch. Pharm.*, 1900, 238, 4—8).—When a potassium alkylthiosulphonate is mixed with the hydrochloride of an alkaloid in aqueous solution, the alkylthiosulphonate of the alkaloid is precipitated; it may be recrystallised from water if necessary. In this way, the following salts were prepared: *Berberine p-toluenethiosulphonate*, $C_6H_4Me \cdot SO_2 \cdot SH, C_{20}H_{17}O_4N, H_2O$; *β -naphthalenethiosulphonate*, $C_{10}H_7 \cdot SO_2 \cdot SH, C_{20}H_{17}O_4N$; the benzene- and α -naphthalenethiosulphonates were prepared, but not analysed; all these are yellow in colour. *Morphine p-toluenethiosulphonate*,



and the benzene- and β -naphthalene-thiosulphonates were prepared; the two last were not analysed. *Strychnine p-toluenethiosulphonate*, $C_6H_4Me \cdot SO_2 \cdot SH, C_{21}H_{22}O_2N_2$.

The precipitation of berberine by potassium β -naphthalenethiosulphonate is complete, and may be utilised for the estimation of the alkaloid. A dilute aqueous solution of the thiosulphonate is prepared and standardised by titration with *N*/100 iodine with starch as indicator; the berberine is precipitated with an excess of this solution, and the excess estimated by titrating the filtered solution with the iodine. $2I = 2C_{10}H_7 \cdot SO_2 \cdot SK = 2C_{20}H_{17}O_4N$.

C. F. B.

Action of Phenylthiocarbimide on Cytisine, Carpaine, and Conhydrine. By F. M. LITERSCHIED (*Arch. Pharm.*, 1900, 238, 230—240).—Cytisine, as a secondary base, interacts quantitatively with phenylthiocarbimide in alcoholic solution at the ordinary temperature, to yield the *phenylthiocarbamide*, $\text{NHPh}\cdot\text{CS}\cdot\text{N}\cdot\text{C}_{11}\text{H}_{13}\text{ON}$, which crystallises from concentrated alcohol in colourless prisms or opaque, white needles, and melts at 254° ; it is basic in character and yields an *aurichloride*, a *platinichloride*, and a *mercurichloride*, but these could not be obtained pure. It is only partially resolved into phenylthiocarbimide and cytisine by hydrochloric acid (either 25 per cent. or fuming, at the ordinary temperature or at 100°), dilute sulphuric acid, or aniline; in each case, the cytisine isolated was the ordinary *lævo*-variety, no racemisation having occurred. Attempts to convert the phenylthiocarbamide into the corresponding cytisine phenylcarbamide by means of yellow mercuric oxide gave only a trace of a colourless compound, crystallising from ethyl acetate in plates and melting at $146\text{--}147^{\circ}$; not enough was obtained for analysis.

Carpaine phenylthiocarbamide, $\text{NHPh}\cdot\text{CS}\cdot\text{N}\cdot\text{C}_{14}\text{H}_{24}\text{O}_2$, crystallises from absolute alcohol in sheaves of needles, melts at 107° , and is much more easily decomposed than the analogous cytisine derivative; thus auric chloride in the cold regenerates carpaine.

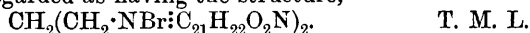
With conhydrine, owing to the small amount of material at the author's disposal, no definite result was obtained. W. A. D.

Carnosine, a New Base present in Meat Extract. By WLADIMIR VON GULEWITSCH and S. AMIRADŽIBI (*Ber.*, 1900, 33, 1902—1903).—The isolation of a new base, *carnosine*, $\text{C}_9\text{H}_{14}\text{O}_3\text{N}_4$, from Liebig's extract of beef, is described; it is very soluble in water, has a strongly alkaline reaction in solution, forms microscopic needles, and melts and decomposes at 239° . The *nitrate*, $\text{C}_9\text{H}_{15}\text{O}_6\text{N}_5$, crystallises from water on adding alcohol in beautiful, stellar aggregates of soft needles, melts and decomposes at 211° , and has $[\alpha]_D + 22.3^{\circ}$ at 20° . The *copper* derivative, $\text{C}_9\text{H}_4\text{N}_4\text{O}_4\text{Cu}$, obtained by boiling the base with copper carbonate, crystallises from water in microscopic, six-sided, hexagonal plates, and decomposes without melting at 220° . The *silver* derivative of carnosine and the acid double salt obtained with silver nitrate closely resemble the corresponding derivatives of arginine. W. A. D.

Morphine. By ALFRED PARTHEIL and A. GRONOVER (*Arch. Pharm.*, 1900, 238, 161—163).—The statement of Hesse (*Abstr.*, 1884, 613) and of Knorr (*Abstr.*, 1889, 417), that methylmorphimethine methohydroxide yields trimethylamine on heating at $170\text{--}180^{\circ}$ is confirmed; the base isolated was characterised by its platinichloride, which melts and decomposes somewhat indefinitely at 220° (Knorr, *loc. cit.*, gives $240\text{--}245^{\circ}$), and by its aurichloride, which melts at $231\text{--}231.5^{\circ}$ (Knorr gives 253° ; Zay, *Abstr.*, 1884, 286, gives 220°). From Vongerichten and Schroetter's results (*Abstr.*, 1882, 1112), it would be expected that dimethylpropylamine would be the decomposition product of methylmorphimethine methohydroxide rather than trimethylamine. W. A. D.

Derivatives of Strychnine. By P. J. TROWBRIDGE (*Arch. Pharm.*, 1900, 238, 241—253).—Strychnine bromoethyl bromide, $C_{21}H_{22}O_2N \cdot NBr \cdot C_2H_4Br$ (Ménétrières, *J. pr. Chem.*, 1862, 85, 230), can be readily converted into the chloride by shaking with freshly precipitated silver chloride; the *aurichloride*, $C_{21}H_{22}O_2N_2(C_2H_4Br)AuCl_4$, forms a yellow precipitate, the *mercurichloride* a white, crystalline precipitate. Strychnine vinyl hydroxide forms a yellow *aurichloride*, $C_{21}H_{22}O_2N_2(C_2H_3)AuCl_4$, and a white, crystalline *mercurichloride*; the *nitrate*, $C_{21}H_{22}O_2N_2(C_2H_3)NO_3$, forms yellowish-white, silky needles, dissolves slightly in cold, but readily in hot water, begins to darken at 250° , and blackens without melting at 280° . By the action of chlorine water on strychnine vinyl chloride, the *additive* compound, $C_{21}H_{22}O_2N_2(C_2H_3Cl_2)Cl$, is produced, but when chlorine gas is used substitution also takes place. By the action of moist silver oxide on the base a certain amount of strychnine is regenerated, but vinylstrychnine is not produced.

Propylene bromide does not combine with strychnine even at 150° , but merely gives a hydrobromide. Trimethylene bromide, however, reacts at the atmospheric temperature and gives an *additive* compound, $2C_{21}H_{22}O_2N_2 \cdot C_3H_6Br_2$, which crystallises from dilute alcohol in white needles containing $4H_2O$, and melts at 297° . The *chloride*, $2C_{21}H_{22}O_2N_2 \cdot C_3H_6Cl_2$, prepared by the action of silver chloride on the bromide, forms white needles readily soluble in water; the *platinichloride* is reddish-yellow and the *aurichloride* lemon-yellow; the *chromate* is a yellow, crystalline precipitate; the *nitrate*, $2C_{21}H_{22}O_2N_2 \cdot C_3H_6(NO_3)_2$, forms colourless, transparent needles, and the *sulphate*, $2C_{21}H_{22}O_2N_2 \cdot C_3H_6SO_4$, white flakes. The additive compound of strychnine and trimethylene bromide, unlike that formed from strychnine and ethylene bromide, is thus the dibromide of a diacid base and is regarded as having the structure,



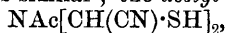
Action of Sulphur Dioxide and Hydrogen Sulphide on Pyridine. By GUSTAVE ANDRÉ (*Compt. rend.*, 1900, 130, 1714—1716. Compare *Abstr.*, 1898, ii, 501).—The *compound*, $C_5NH_5SO_2$, produced by the direct union of dry sulphur dioxide and pyridine, forms yellow, deliquescent lamellæ which readily undergo decomposition. When zinc is placed in contact with pyridine saturated with sulphur dioxide, the metal becomes gradually covered with a white deposit which dissolves in hydrochloric acid with liberation of sulphur dioxide and sulphur; the filtrate from a suspension of this white substance in a saturated solution of hydrogen sulphide, when evaporated in a vacuum, deposits a crystalline substance having a composition corresponding with that of a pyridine trithionate, $(C_5NH_5)_2H_2S_3O_6$.

Pyridine tetrathionate, $(C_5NH_5)_2H_2S_4O_6$, prepared by saturating pyridine successively with sulphur dioxide and hydrogen sulphide, treating the product with alcohol, and allowing the filtered extract to crystallise, separates in colourless, deliquescent lamellæ which dissolve in water or alcohol; at 135° , it melts to a clear liquid which rapidly turns yellow and evolves sulphur dioxide. The solution obtained by decomposing the tetrathionate with well cooled dilute potassium

hydroxide solution deposits only potassium trithionate and traces of sulphur.

Pyridine trithionate, $(C_5NH_5)_2H_2S_3O_6$, obtained in transparent crystals when sulphur dioxide and hydrogen sulphide are passed into a mixture of pyridine with its own weight of water, dissolves in water or alcohol and decomposes at 105° , giving off sulphur dioxide. G. T. M.

Chrysean. By GUSTAF HELLSING (*Ber.*, 1900, 33, 1774—1781. Compare Abstr., 1899, i, 563).—When heated, chrysean darkens at 200° and melts and decomposes at 204° ; it is decomposed also when boiled with dilute acids or alkalis, and is oxidised by nitric acid to sulphuric and oxalic acids. With potassium permanganate, oxalic acid and sulphur are obtained, whilst with potassium ferricyanide or ferric chloride amorphous products are formed, and the same holds true with chlorine, bromine, or iodine. The *copper* derivative of chrysean, $Cu(C_4H_4N_3S_2)_2$, forms microscopic, olive-brown prisms, and crystallises from water, with $4H_2O$, in slender, bright brown needles; the *mercurichloride*, $C_4H_5N_3S_2.HgCl_2$, forms lustrous, yellowish-brown needles, and the *picrate* is similar; the *acetyl* derivative,



crystallises from alcohol, in which it is easily soluble, in small, four-sided, lustrous, golden plates, begins to decompose at 214° and melts at 237° .

Chrysean condenses with aldehydes to form substances of the type, $NH \begin{smallmatrix} CH(CN) \cdot S \\ CH(CN) \cdot S \end{smallmatrix} CHR$, derived from the nucleus, $NH \begin{smallmatrix} CH_2 \cdot S \\ CH_2 \cdot S \end{smallmatrix} CH_2$, to which the name *dihydrodithiazine* is assigned; aromatic ketones, however, are without action on chrysean, although acetone yields a crystalline derivative. The condensation products are relatively unstable, being resolved into their components on boiling with water, dilute acids, or alkalis.

4-Phenyl-2 : 6-dicyanodihydrodithiazine, $NH \begin{smallmatrix} CH(CN) \cdot S \\ CH(CN) \cdot S \end{smallmatrix} CHPh$,

obtained by warming benzaldehyde (1 mol.) with chrysean in alcoholic solution, crystallises from alcohol in golden scales and melts and decomposes at $183-184^\circ$.

4-p-isoPropylphenyl-2 : 6-dicyanodihydrodithiazine, $C_{14}H_{15}N_3S_2$, obtained similarly by using cumaldehyde, crystallises from alcohol in small, slender, yellow needles and melts and decomposes at 118° . Salicylaldehyde yields **4-o-hydroxyphenyl-2 : 6-dicyanodihydrodithiazine**, $C_{11}H_9ON_3S_2$, which crystallises in long, lustrous, golden needles and melts and decomposes at 187° ; the analogous *furfuryl* derivative forms small, four-sided, brown scales and melts and decomposes at 184° . Chrysean dissolved in acetic anhydride interacts vigorously with acetone to form **1-acetyl-4 : 4-dimethyl-2 : 6-dicyanodihydrodithiazine**, which forms brown scales and melts and decomposes at 216° .

The silver and lead derivatives of chrysean are unstable, readily giving rise to the corresponding metallic sulphide and a derivative of *anthiotetrade*, $CH_2 \begin{smallmatrix} N \\ S \end{smallmatrix} CH$.

2:4-Dicyanodihydroazthiotetride, $\text{NH} \begin{smallmatrix} \text{CH}(\text{CN}) \\ \text{CH}(\text{CN}) \end{smallmatrix} \text{S}$, obtained by boiling chrysean suspended in water with silver sulphate, separates in slender, felted, yellowish-white needles which melt at 103° , and rapidly become red owing to the action of light; it yields a white, crystalline double salt, $\text{C}_4\text{H}_3\text{N}_3\text{S}, \text{AgNO}_3$, with silver nitrate, a bright yellow mercurichloride, and an acetyl derivative, $\text{NaC}[\text{CH}(\text{CN})]_2\text{S}$, which crystallises from alcohol in lustrous, white needles. With hydroxylamine, it yields the aminoxime, $\text{CN} \cdot \text{C}_2\text{H}_3\text{NS} \cdot \text{C}(\text{NH}_2) : \text{N} \cdot \text{OH}$, which crystallises from alcohol in bright yellow needles and explodes at 166° ; the foregoing acetyl derivative similarly yields 2-cyano-1-acetyldihydroazthiotetride-4-aminoxime, which crystallises in short, bright yellow, rhombic prisms, and melts and decomposes at 218° . The diacetyl derivative, $\text{CH}(\text{CN}) \begin{smallmatrix} \text{NAc} \\ \text{S} \end{smallmatrix} \text{CH} \cdot \text{C}(\text{NHAc}) : \text{N} \cdot \text{OH}$, prepared from 2-cyanodihydroazthiotetride-4-aminoxime, forms slender, bright yellow needles; it melts at 94° and, after solidification, at 165° , but after again solidifying it melts and decomposes at 237° . The triacetyl derivative, $\text{CH}(\text{CN}) \begin{smallmatrix} \text{NAc} \\ \text{S} \end{smallmatrix} \text{CH} \cdot \text{C}(\text{NHAc}) : \text{N} \cdot \text{OAc}$, crystallises in transparent rhombohedra, melts at 170° , and after solidifying melts and decomposes at 230° . W. A. D.

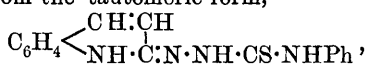
Quinoline Methiodide. By WILHELM MARCKWALD and ERWIN MEYER (*Ber.*, 1900, 33, 1884).—Since great pressure is generated within the sealed vessel used for preparing quinoline methiodide by La Coste's method (*Abstr.*, 1882, 980), and since this is often accompanied by an explosion, the methiodide is more conveniently obtained in quantity by carrying out the reaction in an open vessel fitted with a reflux apparatus. The substance formerly described as quinoline methiodide (m. p. 72°) is in reality the hydrate, $\text{C}_{10}\text{H}_{10}\text{NI}, \text{H}_2\text{O}$; the anhydrous substance melts at 133° and crystallises unchanged from absolute alcohol, but from dilute alcohol the foregoing hydrate separates. W. A. D.

2-Quinolylhydrazine and its Derivatives. By WILHELM MARCKWALD and ERWIN MEYER (*Ber.*, 1900, 33, 1885—1895).—2-Quinolylhydrazine, $\text{C}_9\text{NH}_6 \cdot \text{NH} \cdot \text{NH}_2$, prepared by heating 2-chloroquinoline with an excess of hydrazine hydrate for 6 hours at 140° , separates from water or benzene in large crystals and melts at 134 — 135° ; it is a monacid base, and yields easily soluble salts. The platinichloride, $(\text{C}_9\text{H}_9\text{N}_3)_2, \text{H}_2\text{PtCl}_6$, and the picrate, $\text{C}_{15}\text{H}_{12}\text{N}_6\text{O}_7$, form sparingly soluble crystals and melt and decompose at 170° and 187° respectively.

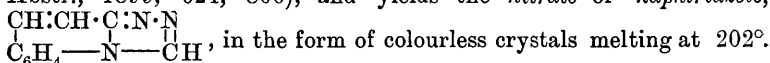
Benzylidene-2-quinolylhydrazine, $\text{C}_9\text{NH}_6 \cdot \text{NH} \cdot \text{N} : \text{CHPh}$, forms yellow crystals, melts at 151° , and yields a sparingly soluble platinichloride melting at 185 — 186° , a dichromate melting and decomposing at 220° , and a picrate melting at 198° . When 2-quinolylhydrazine is left with ethyl oxalate dissolved in alcohol for several hours in the cold, the hydrazide, $\text{C}_9\text{NH}_6 \cdot \text{NH} \cdot \text{NH} \cdot \text{CO} \cdot \text{CO}_2\text{Et}$, separates in yellow, feathery crystals melting at 174 — 175° ; at 150° , oxal-di-2-quinolylhydrazide, $\text{C}_2\text{O}_2(\text{NH} \cdot \text{NH} \cdot \text{C}_9\text{NH}_6)_2$, is obtained as a white, sparingly soluble, crystalline powder melting at 251° .

2-Quinolylsemicarbazide, $C_9NH_6 \cdot NH \cdot NH \cdot CO \cdot NH_2$, obtained by digesting 2-quinolylhydrazine hydrochloride with aqueous potassium cyanate at 100° , forms nodular crystals and melts at 202° ; the *platinichloride* and *picrate* are sparingly soluble, the latter melting at 189° .

The *phenylthiosemicarbazide*, $C_9NH_6 \cdot NH \cdot NH \cdot CS \cdot NHPh, H_2O$, obtained by dissolving phenylthiocarbimide and 2-quinolylhydrazine in 95 per cent. alcohol, forms yellowish crystals, melts at 106° , subsequently resolidifies, and finally melts again at 260° ; the anhydrous phenylthiosemicarbazide, prepared by carrying out the same condensation in dry benzene, forms dark yellow crystals which melt initially at 144° , finally at 260° , and absorb moisture from the air to form the foregoing hydrate; the *picrate* melts at 168 – 169° . The substance melting at 260° , formed on heating either phenylthiosemicarbazide or its hydrate above the melting point, appears to be a *naphtriazolylmercaptan*, $\begin{array}{c} CH:CH:C:N \\ | \quad | \quad | \\ C_6H_4 - N - C - SH \end{array}$, formed by the loss of aniline (1 mol.) from the tautomeric form,

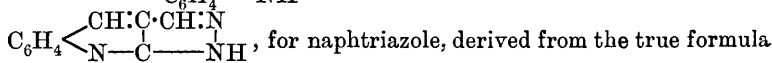


of the parent thiosemicarbazide. When heated with dilute nitric acid, the mercaptan loses its sulphur (compare Wohl and Marckwald, Abstr., 1899, 624, 866), and yields the *nitrate* of *naphtriazole*,



Naphtriazole, obtained by the action of concentrated alkali hydroxides on the nitrate, crystallises from water in long, white needles, and melts at 175° ; it is best prepared by boiling 2-quinolylhydrazine with anhydrous formic acid. The 2-quinolylhydrazine here behaves as its

tautomeride, $\begin{array}{c} CH:CH:C:N \cdot NH_2 \\ | \quad | \quad | \\ C_6H_4 - NH \end{array}$; the alternative configuration,



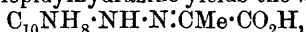
for *naphtriazole*, derived from the true formula for 2-quinolylhydrazine, would make it an analogue of indazole, but this view is untenable, since, unlike the latter, it fails to yield a nitroso-derivative with nitrous acid. *Naphtriazole* is neutral to litmus, and yields salts with an acid reaction in aqueous solution; the *platinichloride*, $(C_{10}H_7N_3)_2 \cdot H_2PtCl_6$, forms orange-red crystals and melts at 323° ; the *dichromate* blackens at 300° without melting, whilst the *argentonitrate* forms white crystals, and melts and decomposes at 239° .

Naphtetrazole, $\begin{array}{c} CH:CH:C:N \\ | \quad | \quad | \\ C_6H_4 - N \cdot N \end{array} \gg N$, is obtained in theoretical amount on adding aqueous sodium nitrite to a cold acetic acid solution of 2-quinolylhydrazine; it forms white crystals, melts at 157° , and is oxidised quantitatively by aqueous potassium permanganate to tetrazole, CH_2N_4 , and carbon dioxide.

2-Hydrazoquinoline, $N_2H_2(C_9NH_6)_2$, is always formed in the preparation of 2-quinolylhydrazine, unless a large excess of hydrazine hydrate is present; it differs from the hydrazine in being insoluble in

boiling water, and separates from dilute acetic acid in yellow crystals melting at 229° . It is a diacid base; the *dihydrochloride* forms sparingly soluble needles melting at 263° , and the *dipicrate* yellow crystals melting and decomposing at 244° . The hydrazo-compound is not acted on by stannous chloride or by zinc dust and acetic acid, but is reduced by boiling with zinc dust and hydrochloric acid to 2-aminoquinoline, the *aurichloride* of which melts at 263° . 2-Azoquinoline, $N_2(C_9NH_6)_2$, obtained by passing nitrogen trioxide into 2-hydrazoquinoline dissolved in 50 per cent. acetic acid, melts at $230-231^{\circ}$, sublimes without decomposition, and is a weak base, its salts being decomposed by water; the *dichromate*, $(C_{18}H_{12}N_4)_2 \cdot H_2Cr_2O_7$, decomposes at 300° , and the *platinichloride*, $C_{18}H_{12}N_4 \cdot H_2PtCl_6$, behaves similarly. W. A. D.

2-Lepidylhydrazine and 4-Quinaldylhydrazine. By WILHELM MARCKWALD and M. CHAIN (*Ber.*, 1900, **33**, 1895—1899. Compare preceding abstract).—2-Lepidylhydrazine, $C_9NH_5Me \cdot NH \cdot NH_2$, prepared by heating 2-chlorolepidine with an excess of hydrazine hydrate for 5 hours at 150° , crystallises from boiling water, melts at $145-147^{\circ}$, and is a monacid base; the *hydrochloride* and *platinichloride* are sparingly soluble in water. The *benzylidene* derivative, $C_{10}NH_8 \cdot NH \cdot N : CHPh$, obtained by means of benzaldehyde, forms slender, lustrous crystals, melts at 150° , and yields a crystalline *dichromate*, $(C_{17}H_{15}N_3)_2 \cdot H_2Cr_2O_7$. With pyruvic acid, 2-lepidylhydrazine yields the *hydrazone*,

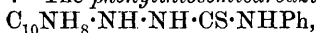


which melts at 215° and crystallises from dilute acid with $3H_2O$, the crystals softening completely at 105° . 2-Lepidylsemicarbazide, obtained by the interaction of potassium cyanate and 2-lepidylhydrazine hydrochloride, separates from alcohol, in which it is sparingly soluble, in yellow crystals, and melts at 215° when rapidly heated. The *phenylthiosemicarbazide*, $C_{10}NH_8 \cdot NH \cdot NH \cdot CS \cdot NHPh$, forms yellow crystals, and, when heated at 180° (compare *loc. cit.*), loses aniline and yields *methylnaphthriazolylmercaptan*, $CMe \begin{array}{c} \text{CH} - \text{C} : \text{N} \\ | \quad | \\ \text{C}_6\text{H}_4 \cdot \text{N} - \text{C} : \text{SH} \end{array}$ which is

sparingly soluble in all solvents, but separates from alcohol in white crystals melting at 280° . *Methylnaphhtetrazole*, $CMe \begin{array}{c} \text{CH} - \text{C} : \text{N} \\ | \quad | \\ \text{C}_6\text{H}_4 \cdot \text{N} \cdot \text{N} \end{array} \text{N}$, forms white crystals and melts at 207° . 2-Hydrazolepidine, $N_2H_2(C_{10}NH_8)_2$, formed during the interaction of 2-chlorolepidine and hydrazine hydrate, when the latter is not present in excess, is sparingly soluble in all solvents, but separates from very dilute acetic acid in yellow crystals, melts at $265-270^{\circ}$, and yields a *dihydrochloride*, $C_{20}H_{18}N_4 \cdot 2HCl$, which forms white needles, and is partially dissociated on washing with water; on reduction with zinc dust and hydrochloric acid, the hydrazo-compound yields 2-aminolepiline, and, on oxidation with nitrogen trioxide, 2-azolepidine, $N_2(C_{10}HN_8)_2$, which separates from alcohol in vermilion crystals, melts at 235° , and yields a crystalline *picrate*. 2-Azolepidine, when heated with hydrochloric acid, is reduced to 2-hydrazolepidine with evolution of chlorine; in this respect it differs from 2-azoquinoline, which is not acted on under the same conditions.

4-Quinaldylhydrazine, $C_{10}H_{11}N_3$, is the sole product of the interaction

of 4-chloroquinaldine and hydrazine hydrate at 150°, no hydrazo-compound being formed; it crystallises from water in stellar aggregates, melts at 117—118°, and yields two crystalline *hydrochlorides*, $C_{10}H_{11}N_3 \cdot HCl$ and $C_{10}H_{11}N_3 \cdot 2HCl$, the latter being converted into the former on heating at 100°, or on being kept in a desiccator over potassium hydroxide. *Benzylidene-4-quinaldylhydrazine*, $C_{17}H_{15}N_3$, separates from alcohol in yellowish crystals, and melts at 161—162°; its *picrate* melts at 130°. *Pyruvic acid 4-quinaldylhydrazone* forms yellow crystals and melts at 197°. The *phenylthiosemicarbazide*,



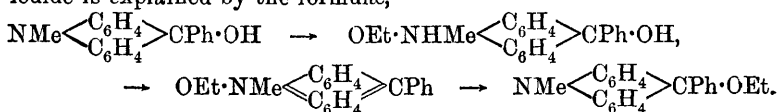
prepared from 4-quinaldylhydrazine, melts at 139°.

W. A. D.

Py-Benzylisoquinolines. By LEOPOLD RÜGHEIMER (*Ber.*, 1900, 33, 1719—1720).—By the action of benzaldehyde on benzoyltetrahydroisoquinoline, two compounds are produced, 4-benzylisoquinoline melting at 117·5—118°, and 3-benzylisoquinoline melting at 103·5°. 1-Benzylisoquinoline is produced by heating isoquinoline with benzyl alcohol at 300°, and melts at 50—52°.

T. M. L.

Ammonium Compounds. V. Ammonium Alcoholates. By HERMANN DECKER (*Ber.*, 1900, 33, 1715—1718).—The formation of an alcoholate from the pseudo-base obtained from phenylacridine methiodide is explained by the formulæ,



These changes are analogous to those involved in the conversion of the carbinol into salts of the ammonium base, except that the isomeric change of the last stage of the reaction does not take place in the latter case. A similar explanation is given of other analogous cases.

T. M. L.

Phenyldiimine. By WILHELM VAUBEL (*Ber.*, 1900, 33, 1711—1713).—When diazoaminobenzene is reduced with zinc dust in alkaline alcoholic solution, the colouring matter which accompanies it is first destroyed, leaving a pure diazoaminobenzene, which is reduced by further boiling; on acidifying the solution and distilling in a current of steam, *phenyldiimine*, $NPh \cdot NH$, is obtained as a yellow oil with a strong odour of bitter almond oil. It has about the same sp. gr. as aniline, boils at 162—164° with partial conversion into a solid substance, is only slightly soluble in water, but readily soluble in alcohol, ether, or benzene, is acid rather than basic in its properties, is stable in the air, does not explode on heating or by percussion, does not reduce Fehling's solution, and is highly poisonous, producing cramp. Its mol. wt. is 123 (calc. 106) as determined by Victor Meyer's method at the temperature of boiling aniline.

T. M. L.

Composition of Compounds of Magenta with Acidic Colouring Matters. By ALPHONSE SEYEWETZ (*Compt. rend.*, 1900, 130, 1770—1773. Compare this vol., i, 356).—The following nitro-colouring acids, *o*-nitrophenol, 2 : 4-dinitrophenol, picric acid, nitrosoresorcinol, and Martius' yellow which contain only nitroxyl and hydroxyl groups

interact with magenta in molecular proportions, whereas naphthol-yellow S, which also contains a sulphonic group, unites with 2 mols. of the colour base.

Diquinonedioxime, $C_6H_2O_2(N\cdot OH)_2$, and alizarin-yellow A each combine with 1 mol. of rosaniline, although they contain 2 and 3 hydroxyl groups respectively.

In the phthalein series, both hydroxyl and carboxyl groups take part in the formation of the lake, 1 mol. of uranin, eosin, or erythrosin combining with 2 mols. of the colour base.

Pararosolic acid and chrome-blue unite with rosaniline in molecular proportions, whereas 3 mols. of the base are required to saturate 1 mol. of chrome-violet.

The alizarin colouring matters all form salts containing 1 mol. of rosaniline, lakes of this type having been obtained from alizarin, alizarin-red S, alizarin-orange, aminoalizarin, and alizarin-blue.

G. T. M.

New Blue Dyes of the Thiazine Series. By W. G. SCHAPOSCHNIKOFF (*J. Russ. Phys. Chem. Soc.*, 1900, 32, 230—248).—When thiodiphenylamine is nitrated, a mixture of mono- and dinitro-derivatives is obtained, which Bernthsen (*Abstr.*, 1886, 53) was unable to separate. The author finds that the mononitro-compound is only slightly soluble in glacial acetic acid, whilst the dinitro-derivative and any unchanged thiodiphenylamine are readily dissolved. By this means the pure *p*-nitrodiphenylamine sulphoxide, $NO_2\cdot C_6H_3\langle\begin{smallmatrix} NH \\ SO \end{smallmatrix}\rangle C_6H_4$, is obtained; it separates from acetic acid in thin, sulphur-yellow scales melting and decomposing at 259° . On reduction in hydrochloric acid solution with stannous chloride and tin, this compound yields aminothiodiphenylamine; the double salt of the latter with zinc chloride forms well-developed, lustrous, white needles or plates, which, when dry, are fairly stable, the rapid oxidation of Bernthsen's preparation being probably due to the presence of a diamino-derivative. When the zinc chloride compound of this pure aminothiodiphenylamine is oxidised by means of ferric chloride, iminothiodiphenylimine is obtained, the corresponding double salt of which dissolves in water, giving a pure blue colour; if any diamino-compound were present, a violet coloration would be obtained, due to the formation of thionine (Lauth's violet) in the reduction product. Iminothiodiphenylimine gives a *dichromate*, $(C_{12}H_8N_2S)_2Cr_2O_7$, and a *platinichloride*, $(C_{12}H_8N_2S)_2H_2PtCl_6$. Koch and Bernthsen's acetyl derivative of thionine (*loc. cit.*) could not be obtained. Iminothiodiphenylimine reacts readily with primary and secondary amines, and less easily with tertiary amines, with the formation of blue dyes. Compounds were obtained with the following amino-compounds: Methyl-, ethyl-, and benzyl-amines, aniline, *o*- and *p*-toluidines, *m*-xylidine, *o*-anisidine, *p*-phenetidine, *o*-, *m*-, and *p*-chloroanilines, α - and β -naphthylamines, diaminoazobenzene, benzidine, dianisidine, tolidine, *m*- and *p*-aminoacetylanilides, *m*-tolylenediamine, methyl-, ethyl-, and benzyl-*m*-tolylenediamines; dimethyl- and diethyl-amines, piperidine, methylaniline, ethylaniline, ethyl-*o*-toluidine, ethyl- and benzyl- α -naphthylamines; trimethylamine, dimethylaniline, diethylaniline, dimethyl-*o*-toluidine, dimethyl-*p*-toluidine. All the bases obtained are blue, the

tints varying from violet to greenish ; they dye silk, wool, and cotton, the colours obtained being stable to light, acids, and soap.

Phenylthionine, $N \begin{smallmatrix} \swarrow \\ \searrow \end{smallmatrix} \begin{smallmatrix} C_6H_3(NH) \\ C_6H_3(NHPh) \end{smallmatrix} \begin{smallmatrix} \nearrow \\ \nwarrow \end{smallmatrix} S$, gives, with sodium chloride, potassium nitrate, bromide or iodide, or zinc chloride, crystalline dye-stuffs having metallic lustre ; all these salts are readily soluble in hot water, and still more so in alcohol or acetic acid, and the alcoholic solutions do not exhibit fluorescence ; they all melt with decomposition, and for the most part contain water of crystallisation. By the action of alkali hydroxide, the salts yield the base, which, with ether or benzene, gives non-fluorescent, carmine-red solutions, whilst it is slightly soluble in water with the formation of a violet colour. The following salts were analysed : the monohydrated *hydrochloride* ; the *platinichloride*, which, like the aurichloride, is insoluble in water ; and the monohydrated *hydrobromide*, *nitrate*, and *dichromate*.

o-Tolylthionine, $C_{19}H_{16}N_3S$, combines with salts, forming double compounds which, in aqueous solutions, have a greener tint than the corresponding phenyl derivatives ; the *nitrate* crystallises with 1 mol. of water.

as-Dimethylthionine, already prepared by Bernthsen (Abstr., 1889, 775) by oxidising dimethylindaminethiosulphonic acid, forms a *platinichloride* and *dichromate*, both readily soluble in hot water. On heating, the dichromate decomposes with the formation of aminothiodiphenyl-

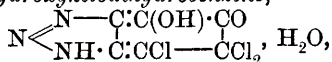
imine dichromate and a compound of the structure $N \begin{smallmatrix} \swarrow \\ \searrow \end{smallmatrix} \begin{smallmatrix} C_6H_3(NH) \\ C_6H_3(OH) \end{smallmatrix} \begin{smallmatrix} \nearrow \\ \nwarrow \end{smallmatrix} S$.

From solutions of its salts, cold sodium hydroxide solution precipitates the base, the aqueous solution of which dyes to a violet colour ; ethereal solutions of the base have an orange-red colour, with a faint greenish fluorescence. On boiling with sodium hydroxide solution, the base is converted into dimethylthionoline and thionol. T. H. P.

Ketochlorides and Quinones of Heterocyclic Compounds, and their Products of Change. Ketochlorides and Quinones of **Aziminobenzene**. By THEODOR ZINCKE, F. STOFFEL, and E. PETERMANN (*Annalen*, 1900, 311, 276—329. Compare Abstr., 1898, i, 537).—

Aziminotetrachloroketodihydrobenzene, $N \begin{smallmatrix} \swarrow \\ \searrow \end{smallmatrix} \begin{smallmatrix} N-C:CCl-CO \\ NH \cdot C:CCl \cdot CCl_2 \end{smallmatrix}$, prepared from aziminoaminobenzene by the action of chlorine, forms a yellow, viscous oil, but may be obtained in crystals by reduction to aziminotrichlorophenol, followed by chlorination of this compound ; it crystallises from benzene in yellowish plates, which become opaque in a vacuum, and melts at 171° , beginning to blacken at 140° .

Aziminotrichlorohydroxyketodihydrobenzene,



produced by the action of boiling water on the foregoing substance, forms small, colourless plates, which shrink at 100° , afterwards becoming red, and finally decompose at 260° with detonation ; the development of a red colour on heating is due to conversion into aziminodichloro-*o*-quinone, which arises from elimination of water and hydrogen chloride.

Aziminotrichlorophenol, $N \begin{smallmatrix} \diagup \\ \diagdown \end{smallmatrix} \begin{smallmatrix} N-C \cdot CCl \cdot C \cdot OH \\ NH \cdot C \cdot CCl \cdot CCl \end{smallmatrix}$, obtained by reducing aziminotetrachloroketodihydrobenzene with stannous chloride and concentrated hydrochloric acid, crystallises in small, colourless, prismatic needles containing $1H_2O$, and melts at 260° , becoming anhydrous at 135° ; the *diacetyl* derivative melts above 300° .

Aziminodichlorophenol, $N \begin{smallmatrix} \diagup \\ \diagdown \end{smallmatrix} \begin{smallmatrix} N-C \cdot CCl \cdot C \cdot OH \\ NH \cdot C \cdot CH \cdot CCl \end{smallmatrix}$, is associated with the foregoing substance in the reduction of the tetrachloroketone, and may be obtained by evaporating the mother liquor and precipitating it with water; the compound forms small, colourless needles, which melt and decompose at 212° .

Aziminodichloro-o-quinone, $N \begin{smallmatrix} \diagup \\ \diagdown \end{smallmatrix} \begin{smallmatrix} N-C \cdot CO \cdot CO \\ NH \cdot C \cdot CCl \cdot CCl \end{smallmatrix}$, prepared by heating a solution of aziminotrichlorophenol in glacial acetic acid with a small proportion of concentrated nitric acid, is also formed when the tetrachloroketone is heated with water or nitric acid; it crystallises from glacial acetic acid in red needles belonging to the hexagonal system, and gradually blackens when heated, detonating above 260° . As already stated, the quinone is produced when aziminotrichlorohydroxyketodihydrobenzene is heated alone, or with nitric or sulphuric acid. The *azine*, $C_{12}H_5N_5Cl_2$, produced by the action of *o*-phenylenediamine, crystallises from glacial acetic acid in small, yellow needles, and decomposes gradually above 260° .

Aziminooanilinochlorohydroxy-p-quinone, $N \begin{smallmatrix} \diagup \\ \diagdown \end{smallmatrix} \begin{smallmatrix} N-C \cdot CO \cdot C \cdot OH \\ NH \cdot C \cdot C(NPh) \cdot CCl \end{smallmatrix}$, obtained by heating an alcoholic solution of aziminodichloro-o-quinone with aniline, dissolves very sparingly in ordinary solvents, and does not melt below 300° ; hot hydrochloric acid resolves it into the hydrochloride of the aniline derivative of aziminochlorohydroxy-p-quinone, which is described below.

Aziminodichlorocatechol, $N \begin{smallmatrix} \diagup \\ \diagdown \end{smallmatrix} \begin{smallmatrix} N-C \cdot C(OH) \cdot C \cdot OH \\ NH \cdot C \cdot CCl \cdot CCl \end{smallmatrix}$, formed by reducing aziminodichloro-o-quinone and aziminotrichlorohydroxyketodihydrobenzene, crystallises from glacial acetic acid in lustrous, white prisms containing 2 mols. of the solvent; it decomposes gradually above 260° . The *acetyl* derivative melts at 203° .

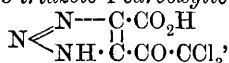
Aziminochlorohydroxy-p-quinone, $N \begin{smallmatrix} \diagup \\ \diagdown \end{smallmatrix} \begin{smallmatrix} N-C \cdot CO \cdot C \cdot OH \\ NH \cdot C \cdot CO \cdot CCl \end{smallmatrix}$, prepared by heating aziminooanilinochlorohydroxy-p-quinone with alcoholic hydrochloric acid, and treating the resulting aniline compound with boiling water, crystallises from glacial acetic acid in deep yellow, lustrous rhombohedra, which contain acetic acid, and detonates at $230-231^\circ$; the *sodium* salt crystallises in deep violet to reddish-brown needles containing $2H_2O$, and the *silver*, *copper*, *lead*, *barium*, and *calcium* salts are of the same colour, but insoluble in water. The *anilino*-compound, $C_{18}H_{16}O_3N_5Cl$, obtained by heating aziminochlorohydroxy-p-quinone in alcohol with excess of aniline, crystallises in small, reddish-brown needles, and gives up all its aniline when heated.

Hydrochloric acid converts it into the *hydrochloride* of the anilino-compound, $C_{12}H_9O_3N_4Cl$; this crystallises from glacial acetic acid in groups of golden yellow prisms, which blacken and decompose at 179° . This substance is produced by the action of hydrochloric acid on aziminoanilinochlorohydroxy-*p*-quinone, and, on treatment with boiling water, yields aziminochlorohydroxy-*p*-quinone. *o*-Phenylenediamine does not give rise to the expected eurhodol, but yields two compounds having the composition $C_{12}H_6ON_5Cl$ and $C_{18}H_9N_7$ respectively.

Aziminotetraketotetrahydrobenzene, $N \begin{smallmatrix} \diagup \\ \diagdown \end{smallmatrix} \begin{smallmatrix} N-C \cdot CO \cdot CO \\ NH \cdot C \cdot CO \cdot CO \end{smallmatrix}$, produced by the action of concentrated nitric acid on aziminochlorohydroxy-*p*-quinone dissolved in glacial acetic acid, crystallises from glacial acetic acid containing nitric acid in small, transparent, lustrous needles containing $2H_2O$, which gradually darken above 130° , and finally detonate at about 190° . The *diazine*, $C_{18}H_9N_7$, formed by the action of *o*-phenylenediamine, dissolves very sparingly in ordinary solvents, and does not change below 260° .

Aziminodihydroxy-p-quinone, $N \begin{smallmatrix} \diagup \\ \diagdown \end{smallmatrix} \begin{smallmatrix} N-C \cdot CO \cdot C \cdot OH \\ NH \cdot C \cdot CO \cdot C \cdot OH \end{smallmatrix}$, is prepared by dissolving the tetraketone in a solution of sodium carbonate and passing carbon dioxide through the liquid while heated on the water-bath during a short period, the deep blue solution being then acidified carefully with hydrochloric acid. It crystallises from glacial acetic acid or methyl alcohol as a brick-red powder containing $1H_2O$, and does not melt at 260° , although it darkens below this temperature.

5-Trichloroacetyl-1:2:3-triazole-4-carboxylic acid,



resulting from the action of bleaching powder on aziminotrichlorophenol, aziminodichloro-*o*-quinone, and aziminochlorohydroxy-*p*-quinone, is best prepared from the dichloroquinone; it separates from wet ether in yellow crystals containing $3H_2O$, which become anhydrous at 100° . The *phenylhydrazone* is orange-red, and melts at 247° , when it decomposes.

5-Trichloroacetyl-1:2:3-triazole, $N \begin{smallmatrix} \diagup \\ \diagdown \end{smallmatrix} \begin{smallmatrix} N-CH \\ NH \cdot C \cdot CO \cdot CCl_3 \end{smallmatrix}$, obtained by heating the carboxylic acid, crystallises from water in slender, colourless needles and melts at 129° . Sodium hydroxide eliminates chloroform, and produces *1:2:3-triazole-4-carboxylic acid*, $N \begin{smallmatrix} \diagup \\ \diagdown \end{smallmatrix} \begin{smallmatrix} N-CH \\ NH \cdot C \cdot CO_2H \end{smallmatrix}$, which crystallises from hydrochloric acid in transparent rhombohedra and melts at 220° , when carbon dioxide is eliminated, and *1:2:3-triazole (pyrro-a-b-diazole)*, $N \begin{smallmatrix} \diagup \\ \diagdown \end{smallmatrix} \begin{smallmatrix} N-CH \\ NH \cdot CH \end{smallmatrix}$, produced.

1:2:3-Triazole-4:5-dicarboxylic (aziminoethylenedicarboxylic) acid, $N \begin{smallmatrix} \diagup \\ \diagdown \end{smallmatrix} \begin{smallmatrix} N-C \cdot CO_2H \\ NH \cdot C \cdot CO_2H \end{smallmatrix}$, prepared by the action of a 10 per cent. solution of sodium hydroxide on trichloroacetyl-1:2:3-triazolecarboxylic acid,

has been already obtained by Bladin (Abstr., 1894, i, 76), and by Zincke and Helmert (Abstr., 1896, i, 550); it is also produced during the oxidation of aziminochlorohydroxy-*p*-quinone to the tetraketone.

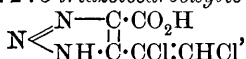
When a 10 per cent. solution of sodium hydroxide acts on aziminodichloro-*o*-quinone, the dichloroketocarboxylic acid,
$$\text{N} \begin{array}{c} \diagup \text{N} - \text{C} \cdot \text{CO} \cdot \text{CO}_2\text{H} \\ \diagdown \text{NH} \cdot \text{C} \cdot \text{CCl} : \text{CHCl} \end{array}$$
 is produced, crystallising from dilute hydro-

chloric acid in lustrous, colourless needles or stout prisms, which contain $1\text{H}_2\text{O}$, and melt, decomposing, at 165° ; the *phenylhydrazone* crystallises from dilute acetic acid in small, yellow needles, which melt and decompose at 182° . The tetrachloroketocarboxylic acid,

$$\text{N} \begin{array}{c} \diagup \text{N} - \text{C} \cdot \text{CO} \cdot \text{CO}_2\text{H} \\ \diagdown \text{NH} \cdot \text{C} \cdot \text{CCl}_2 \cdot \text{CHCl}_2 \end{array}$$
 obtained by the action of chlorine, forms colourless, transparent needles containing $1\text{H}_2\text{O}$, and melts at 167° , evolving gas.

The acid, $\text{C}_6\text{H}_3\text{O}_3\text{N}_3\text{Cl}_2$, prepared by the action of sodium hydroxide on aziminotetrachloroketodihydrobenzene, crystallises from dilute nitric or glacial acetic acid in lustrous, colourless leaflets which melt and decompose at 184° ; the *phenylhydrazone* crystallises in small, yellow needles, which sinter at 182° , and melt, decomposing, at $201\text{--}203^\circ$.

αβ-Dichloroethylene-1 : 2 : 3-triazolecarboxylic acid,



produced on oxidising the foregoing acid with chromic acid or with an alkaline solution of bleaching powder, is also formed when the dichloroketocarboxylic acid from the dichloro-*o*-quinone is oxidised with chromic acid; it forms small, white, lustrous needles, which melt and decompose at $204\text{--}205^\circ$; the *silver* salt is white and crystalline.

Chlorine converts the substance into the acid,
$$\text{N} \begin{array}{c} \diagup \text{N} - \text{C} \cdot \text{CO}_2\text{H} \\ \diagdown \text{NH} \cdot \text{C} \cdot \text{CCl}_2 \cdot \text{CHCl}_2 \end{array}$$
 which crystallises from a mixture of ether and benzene in small, colourless needles and melts and decomposes at 182° ; it also crystallises from dilute nitric acid in leaflets containing $2\text{H}_2\text{O}$. M. O. F.

Aziminole. By THEODOR ZINCKE and PH. SCHWARZ (*Annalen*, 1900, 311, 329—340. Compare Nietzki and Braunschweig, Abstr., 1895, i, 135).—Benzeneaziminole, $\text{C}_6\text{H}_4 \begin{array}{c} \diagup \text{N} \\ \diagdown \text{N}(\text{OH}) \end{array}$, obtained by Nietzki and Braunschweig on treating *o*-nitrophenylhydrazine with alkali, melts at 157° ; reduction with hydriodic acid at $140\text{--}150^\circ$ converts it into the *periodide* of aziminobenzene, $\text{C}_6\text{H}_5\text{N}_3\text{I}_2\cdot\text{HI}$. When benzeneaziminole is warmed with acetyl chloride, a compound is obtained which is identical with the substance produced by the action of phosphorus trichloride; it melts at about 110° , and probably has the constitution $\text{C}_6\text{H}_4 \begin{array}{c} \diagup \text{N} \\ \diagdown \text{NCl} \end{array}$. The result of treating benzeneaziminole with chlorine is somewhat uncertain, and the composition of the product depends largely on the conditions of the experiment.

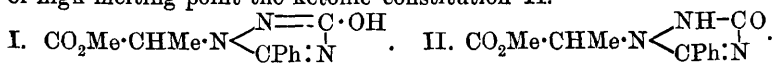
Aziminolethylenedicarboxylic [1-hydroxy-1:2:3-triazole-4:5-dicarboxylic] acid, $\text{N} \begin{smallmatrix} \text{N} \text{---} \text{C} \cdot \text{CO}_2\text{H} \\ \text{N}(\text{OH}) \cdot \text{C} \cdot \text{CO}_2\text{H} \end{smallmatrix}$ prepared by oxidising benzene-aziminole with potassium permanganate, separates from water in large, white crystals containing $2\text{H}_2\text{O}$; it melts at 92° , but if previously dried in the desiccator melts and decomposes at 150° . The *monopotassium* salt and the *disilver* salt contain $1\text{H}_2\text{O}$, and the *diammonium* salt is anhydrous.

Tolueneaziminole, $\text{C}_6\text{H}_3\text{Me} \begin{smallmatrix} \text{N} \\ \text{N}(\text{OH}) \end{smallmatrix} \text{N}$, prepared by the action of alkali on 1:3:4-nitrotolylhydrazine, crystallises from hot water in long, white needles, and melts at 176° , when it decomposes; the *lead* salt is crystalline, and the *silver* salt amorphous. M. O. F.

3-Hydroxy-5-alkyl-1:2:4-triazole-1-propionic Acids. By JAMES R. BAILEY and S. F. ACREE (*Ber.*, 1900, 33, 1520—1537).—A number of acyl derivatives of ethyl semicarbazinopropionate have been prepared by Widman's method (*Abstr.*, 1898, i, 335). As the other derivatives of semicarbazinopropionic acid are insoluble, or sparingly soluble, in the ordinary organic solvents, they do not lend themselves so readily to the preparation of acyl derivatives, and the yields are mostly poor. The acyl derivatives of the ethyl ester are obtained in almost quantitative yield when the ester is treated with an equivalent quantity of an acid chloride dissolved in benzene, chloroform, or ethyl acetate, generally with the addition of potassium or sodium hydrogen carbonate. Hot concentrated acids remove the acyl groups from these compounds, and dilute alkalis, especially when warm, convert them into the corresponding triazoles.

The 3-hydroxy-5-alkyltriazole-1-propionic acids are dibasic, yielding normal and acid salts, and also monoacetyl derivatives. With diazomethane, they yield methyl methoxytriazolecarboxylates, and when esterified by Fischer's method, give esters which are monobasic acids (phenols), and therefore yield salts and acetyl derivatives.

The colour which the triazole compounds give with ferric chloride varies in different circumstances, a difference which is most readily accounted for by a keto-enolic isomerism. Methyl 3-hydroxy-5-phenyltriazole-1-propionate gives a deep colour with ferric chloride, and when placed in a bath heated at 157° , melts, but then solidifies, to again melt at 171° ; if this variety of high melting point is crystallised from alcohol several times, it melts at 173 — 174° , and then gives only the faintest coloration with ferric chloride. It is thought probable that the compound of low melting point has the constitution I, and that of high melting point the ketonic constitution II.



Ethyl benzoylsemicarbazinopropionate,

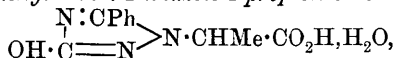


crystallises in hair-like needles, melts at 177° , and is insoluble in ether, benzene, or light petroleum; the *silver* salt, $\text{C}_{13}\text{H}_{15}\text{O}_4\text{N}_3\text{Ag}_2$, has been prepared and analysed.

Benzoylsemicarbazinopropionic acid, obtained by hydrolysing the

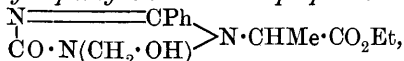
ester with aqueous sodium hydrogen carbonate, crystallises from water in microscopic needles melting and decomposing at 186° ; the *sodium* salt, $C_{11}H_{12}O_4N_3Na$, is extremely hygroscopic, and decomposes above 200° . *Benzoylsemicarbazinopropionitrile* melts and decomposes at about 185° .

3-Hydroxy-5-phenyl-1 : 2 : 4-triazole-1-propionic acid,



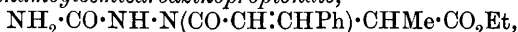
is obtained when any one of the above-mentioned compounds is warmed for some 30 minutes at 50° with 10 per cent. potassium hydroxide; it loses its water of crystallisation at $105-110^{\circ}$, begins to turn red at 225° , melts and decomposes at $239-240^{\circ}$, and is insoluble in all the ordinary solvents, with the exception of alcohol. The *barium* (with $3\text{H}_2\text{O}$), *lead*, *ammonium* (with H_2O), and *calcium* salts have been prepared, also the *hydrochloride*, $C_{11}H_{11}O_3N_3\cdot\text{HCl}$, which crystallises in colourless needles melting at 102° , and is immediately decomposed by water. The *ethyl* ester, $\text{OH}\cdot\text{C}_2\text{N}_3\text{Ph}\cdot\text{CHMe}\cdot\text{CO}_2\text{Et}$, melts at $171-173^{\circ}$, and is readily hydrolysed by alkalis or by barium carbonate. The *sodium*, $C_{13}H_{14}O_3N_3Na$, and *silver* salts have been prepared, as also the *acetyl* derivative melting at 79° , the *benzoyl* derivative melting at $78-79^{\circ}$, and the *methyl ether*, $\text{OMe}\cdot\text{C}_2\text{N}_3\text{Ph}\cdot\text{CHMe}\cdot\text{CO}_2\text{Et}$, which is an oil. When treated with alcoholic ammonia, the ethyl ester is converted into *3-hydroxy-5-phenyltriazole-1-propionamide*, crystallising in long, thin needles which turn red at 240° , and decompose, with rapid evolution of gas, at 274° .

2-Hydroxymethyl-5-phenyl 3-triazolone-1-propionic acid,



obtained by the action of formaldehyde on the triazolepropionic acid, crystallises in thin, prismatic plates melting at 242° and evolving formaldehyde.

Ethyl cinnamoylsemicarbazinopropionate,



is readily soluble in chloroform, alcohol, or ethyl acetate; it softens at 170° and melts at $178-179^{\circ}$. The corresponding *nitrile* melts and decomposes at 233° . *3-Hydroxy-5-styryltriazole-1-propionate* crystallises from alcohol in aggregates of small, glistening needles; it melts and decomposes at $242-243^{\circ}$, and, on oxidation with alkaline permanganate, yields benzoic acid. The *acetyl* derivative, melting and decomposing at 168° , the *hydrochloride*, and the *ammonium* salt, $C_{13}H_{12}O_3N_3\cdot\text{NH}_4$, have been prepared. *Methyl 3-methoxy-5-styryltriazolepropionate*, obtained by the action of an ethereal solution of diazomethane on the acid, is an oil.

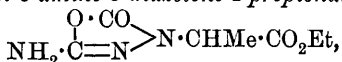
Ethyl acetylsemicarbazinopropionate melts at 141° , and is soluble in water and the ordinary organic solvents with the exception of ether and light petroleum. The corresponding *nitrile* begins to soften below 160° , and melts and decomposes at 164° . *3-Hydroxy-5-methyltriazolepropionic acid* turns brown at 260° , and is completely decomposed at 292° ; it is only very sparingly soluble in water; its *ethyl* ester crystallises in small, flat prisms and melts at 132° . The *methyl*

ester, when crystallised from ethyl acetate, melts at 150—151°, and gives a deep colour with ferric chloride; when precipitated by the addition of light petroleum to its ethyl acetate solution, it melts at 154—155°, and does not give so deep a colour with ferric chloride. The *amide* crystallises in small prisms melting and decomposing at 252°.

Ethyl propionylsemicarbazinopropionate melts at 156°, and is readily soluble in water or alcohol; the corresponding *n*-butyryl compound melts at 148°, the isobutyryl derivative at 182°, the isovaleryl compound at 174°, and the chloroacetyl compound at 135°. *3-Hydroxy-5-ethyltriazole-1-propionic acid* crystallises in needles, blackens at 240°, and decomposes at 258°; it dissolves readily in alcohol and moderately in water. *3-Hydroxy-5-n-propyltriazolepropionic acid* crystallises in needles, decomposes at 249°, and is readily soluble in water; the isopropyl derivative decomposes at about 240°, and the isobutyl compound at 211°; the last substance dissolves in water with the greatest readiness.

Ethyl benzenesulphosemicarbazinopropionate,
 $\text{NH}_2 \cdot \text{CO} \cdot \text{NH} \cdot \text{N}(\text{SO}_2\text{Ph}) \cdot \text{CHMe} \cdot \text{CO}_2\text{Et}$,
 crystallises from alcohol in long prisms and melts at 151°.

Ethyl carboxyethylsemicarbazinopropionate,
 $\text{NH}_2 \cdot \text{CO} \cdot \text{NH} \cdot \text{N}(\text{CO}_2\text{Et}) \cdot \text{CHMe} \cdot \text{CO}_2\text{Et}$,
 melts at 148°. *Ethyl 3-amino-5-diazolone-1-propionate*,



obtained from ethyl semicarbazinopropionate, carbonyl chloride, and sodium hydrogen carbonate, crystallises from water in long needles melting at 57°. *Ethyl 3-amino-5-thiodiazolone-1-propionate* crystallises in needles, melts at 117·5°, and is only sparingly soluble in water.

J. J. S.

Compounds of Diantipyrinemethane (Formopyrine). By GUSTAVE PATEIN (*Bull. Soc. Chim.*, 1900, [iii], 23, 600—605. Compare Abstr., 1898, i, 493).—Formopyrine interacts with iodine in alcoholic solution to form a *tetraiodide*, $\text{CH}_2(\text{C}_{11}\text{H}_{11}\text{ON}_2\text{I}_2)_2$, which crystallises in slender needles possessing the colour and appearance of iodine, melts at about 135°, and is insoluble in water, but more or less soluble in organic solvents; it is decomposed by alkalis or metallic silver with the formation of formopyrine and a metallic iodide.

Formopyrine does not react with phenols directly, but when warmed with catechol in presence of sulphuric acid a *compound*, $(\text{C}_{23}\text{H}_{24}\text{O}_2\text{N}_4, \text{H}_2\text{O})_5[\text{C}_6\text{H}_3(\text{OH})_2 \cdot \text{SO}_3\text{H}]_4 [(\text{OH})_2 : \text{SO}_3\text{H} = 1 : 2 : 3]$, is obtained which forms brilliant, nearly colourless crystals melting at 260—262°, and is decomposed by alkalis with regeneration of formopyrine. Its constitution is shown by the fact that it may also be obtained by the action of formopyrine on catechol-3-sulphonic acid. A similar and isomeric *compound* melting at 220° is obtained from resorcinol, or resorcinol-4-sulphonic acid, and formopyrine, whilst quinol yields a *compound* crystallising in colourless needles melting at 218—220°, which differs from the two preceding derivatives in containing molecular proportions of formopyrine and quinolsulphonic acids.

N. L.

Relationship between Azoxybenzene and Diazobenzene. By EUGEN BAMBERGER (*Ber.*, 1900, 33, 1957—1959. Compare following abstract).—The introduction of a hydroxy-group into azoxybenzene renders it possible to oxidise one ring; the product is in every case an *isodiazotate*, and no normal diazotate could be detected.

T. M. L.

Action of Aqueous Sodium Hydroxide on Nitrosobenzene. By EUGEN BAMBERGER (*Ber.*, 1900, 33, 1939—1957).—By the action of aqueous sodium hydroxide on nitrosobenzene at 100°, the following substances were produced: Azoxybenzene, nitrobenzene, a crystalline substance melting at 242—243°, *o*-aminophenol with a trace of *p*-aminophenol, aniline, *o*-hydroxyazobenzene, *o*-hydroxyazoxybenzene, *iso-o*-hydroxyazoxybenzene, and *p*-hydroxyazoxybenzene.

o-Hydroxyazobenzene, $C_6H_5 \cdot N_2 \cdot C_6H_4 \cdot OH$, crystallises from ether in orange-red, silky needles with a blue metallic lustre, melts at 82·5—83°, is volatile with steam, has a normal molecular weight, and in a saturated aqueous solution (7·57 mg. per litre) gives $K_{25} = 2 \cdot 27 \times 10^{-6}$; the copper salt crystallises from alcohol in reddish-brown, silky needles with a slight green lustre, and melts and decomposes at 225—226°; the phenol is reduced by zinc dust and ammonium chloride to aniline and *o*-aminophenol, thus establishing its constitution.

o-Hydroxyazoxybenzene, $C_6H_5 \cdot N_2O \cdot C_6H_4 \cdot OH$, forms golden-yellow, silky, felted needles, melts at 75·5—76°, is volatile with steam, dissolves in aqueous sodium hydroxide, and less readily in hot sodium carbonate, the latter solution depositing a part of the phenol on cooling; it is oxidised by alkaline permanganate to an *isodiazot*-salt, when reduced yields aniline and *o*-aminophenol, and is converted by strong sulphuric acid into *o*-hydroxyazobenzene.

iso-o-Hydroxyazoxybenzene, isomeric with the preceding compound, forms minute, golden-yellow, silky needles, is volatile with steam, melts at 108—108·5°, dissolves in alkalis, is oxidised to an *isodiazotate*, and when reduced yields aniline and *o*-aminophenol; it has not been ascertained in what respect it differs from the preceding compound.

p-Hydroxyazoxybenzene crystallises from light petroleum or benzene in yellow, silky needles, melts at 156·5°, is much less readily soluble in light petroleum than the preceding compounds, and is not volatile with steam; it dissolves in alkalis, is oxidised by alkaline permanganate to an *isodiazotate*, and reduced to aniline and *p*-aminophenol; it can be prepared synthetically by the action of phenylhydroxylamine on *p*-nitrosophenol.

Nitrosobenzene is only very slowly acted on by aqueous sodium hydroxide in the cold; the product contains a very much larger amount of resin than in the preceding case, and very little nitrobenzene, but a considerable amount of the isomeric *p*-nitrosophenol; the four acids described above are only produced in very small quantities when the reaction takes place in the cold. T. M. L.

Metallic Derivatives of *s*-Dibenzoylhydrazine and the Transformation of Dibenzoylhydrazine into Azodibenzoyl. By ROBERT STOLLÉ and A. BENRATH (*Ber.*, 1900, 33, 1769—1770).—On boiling dibenzoylhydrazine for a short time with alcoholic potass-

ium hydroxide (1 mol.), the *potassium* derivative, N_2HKBz_2 , separates in flat, lustrous needles, sparingly soluble in alcohol; the analogous *silver* derivative is a pale yellow powder, which is not acted on by light, and, on shaking with an ethereal solution of iodine, yields *s*-dibenzoylhydrazine along with *azodibenzoyl*, $NBz:NBz$. The latter crystallises in slender, orange-red needles and melts at $117-118^\circ$, decomposing slightly above this temperature; when boiled with alcohol, a gas is evolved, and the solution, initially coloured, becomes colourless, apparently owing to the reduction of the compound to *s*-dibenzoylhydrazine. W. A. D.

Diazobenzene Nitrate from Nitrosophenylhydrazine. By LEOPOLD RÜGHEIMER (*Ber.*, 1900, **33**, 1718).—When the gases obtained by the action of arsenious acid on nitric acid are passed over solid potassium nitrite into a dilute solution of nitrosophenylhydrazine in dry ether, diazobenzene nitrate separates, and can be purified by dissolving in alcohol and precipitating with ether. T. M. L.

Action of Acyl Cyanoacetic Esters on Benzenediazonium and Diphenyltetrazonium Chlorides. By G. FAVREL (*Compt. rend.*, 1900, **131**, 190—192).—When an ethereal acylcyanoacetate is added to a solution of benzenediazonium chloride containing excess of sodium acetate or sodium tartrate, the acyl radicle is displaced by the diazo-group, and the corresponding fatty acid is eliminated; the product is a crystalline precipitate, consisting of a mixture of the α - and β -ethyl benzeneazocyanoacetates, the one melting at $124-125^\circ$, and the other at $84-85^\circ$. Acetic acid is set free when ethyl acetocyanoacetate is employed, whilst propionic acid is eliminated from the corresponding propionyl derivative. By the action of diphenyltetrazonium chloride on the acylcyanoacetates, α - and β -azo-compounds are similarly obtained, but in this case the reaction is complicated by secondary changes. G. T. M.

Action of Chloroform and Chloral Hydrate on Hæmoglobin. By EMANUEL FORMÁNEK (*Zeit. physiol. Chem.*, 1900, **29**, 416—422).—Both chloroform and chloral hydrate are good precipitants of the blood pigment, particularly at 56° ; although the pigment undergoes but little change, yet this method cannot be used as a means of separating it from the blood, as the other proteids are precipitated also. Bromoform acts similarly, but less vigorously. Some criticisms are added on the results obtained by Arnold, by the use of chloroform in his preparation of neutral hæmatin. W. D. H.

Organic Chemistry.

Composition of Petroleum. By CHARLES F. MABERY (*J. Soc. Chem. Ind.*, 1900, 19, 502—508. Compare Abstr., 1897, i, 449).—*Hydrocarbons in Pennsylvanian Petroleum boiling above 216°*.—The author has isolated the following hydrocarbons from Pennsylvanian petroleum: $C_{13}H_{30}$ [?], boiling at 225—226°; $C_{14}H_{32}$ [?], 237—238°; $C_{15}H_{32}$, 256—257°; $C_{16}H_{34}$, 274—275°; $C_{17}H_{36}$, 288—289°; $C_{18}H_{38}$, 300—301°; $C_{19}H_{40}$, 316°; also members of the paraffin series containing 21, 23, 24, 25, and 26 atoms of carbon respectively. These differ essentially both in melting and boiling points from the corresponding hydrocarbons obtained by Krafft.

Composition of Californian Petroleum. [With EDWARD J. HUDSON].—In the fractions of lower boiling point obtained from various Californian petroleum, large quantities of benzene and its homologues have been met with, together with hexane, hexamethylene, a hydrocarbon C_7H_{14} , probably hexahydrotoluene; C_8H_{16} , boiling at 118—119°, C_9H_{18} , 135°; $C_{10}H_{20}$, 162°; $C_{11}H_{22}$, 196°; and $C_{12}H_{24}$, 216°. The composition of these hydrocarbons was established by analysis and by molecular weight determinations. The chloro-derivatives of all were prepared, analysed, and their molecular weights ascertained. From the distillates with higher boiling points, the compounds $C_{13}H_{26}$ — $C_{19}H_{38}$, $C_{21}H_{42}$, and naphthalene have been isolated.

Composition of Japanese Petroleum. [With S. TAKANO].—Petroleum from different localities vary considerably as regards specific gravity, iodine number, and percentage of nitrogen and sulphur. The amounts of benzene homologues are larger than are contained in Pennsylvanian, but smaller than are found in Californian oil. Six fractions collected between 98° and 216° give numbers corresponding with those required for the general formula C_nH_{2n} ; the fraction boiling at 216° is $C_{12}H_{24}$.

Nitrogen Compounds in Californian Oil.—Californian oils contain a relatively large amount of nitrogen (0.91—2.39 per cent.), but this cannot be accurately estimated by the Kjeldahl method. The bases have been separated by extraction with dilute sulphuric acid, and on subsequent fractional distillation gave the series of compounds $C_{13}H_{17}N$, boiling at 130—140°; $C_{13}H_{18}N$, at 197—199°; $C_{14}H_{19}N$, at 215—217°; $C_{15}H_{19}N$, at 223—225°; $C_{16}H_{19}N$, at 243—245°; and $C_{17}H_{21}N$, at 270—275°. The bases have a high specific gravity and an extremely pungent odour resembling that of nicotine; no well defined salts could be isolated, and on oxidation with chromium trioxide a small amount of acetic acid is the only product. They form additive compounds with ethyl iodide at 110°, and it is thought probable that they are tetrahydroquinoline derivatives. The number of hydrogen atoms is uncertain.

Sulphur Compounds in Canadian Petroleum. [WITH W. O. QUAYLE].—The following compounds have been isolated, the boiling points given being under 50 mm. pressure: $C_7H_{14}S$, at 71—73°; $C_8H_{16}S$, 79—81°; $C_8H_{16}S$, 97—98°; $C_9H_{18}S$, 110—112°; $C_{10}H_{20}S$, 114—116°; $C_{11}H_{22}S$, 129—131°; $C_{14}H_{28}S$, 168—170°; $C_{18}H_{36}S$, 198—200°. Potass-

ium permanganate in acid or alkaline solution converts these compounds into the corresponding sulphones. J. J. S.

Action of Finely Divided Platinum, Cobalt and Iron on Acetylene and Ethylene. By PAUL SABATIER and JEAN B. SENDERENS (*Compt. rend.*, 1900, 131, 267—270. Compare this vol., i, 471).—Finely divided platinum has no action on pure acetylene at the ordinary temperature, but above 150° there is intumescence and the gas is partially decomposed with liberation of carbon and formation of ethylene, together with small quantities of benzene, ethane, and hydrogen.

Cobalt, free from nickel, has no action at the ordinary temperature, but above 200° the gas is almost completely decomposed by it into hydrogen, ethane, and carbon, with a small quantity of benzene and its homologues. Iron behaves similarly, but the proportion of ethane formed is much smaller, and the chief products in addition to hydrogen and carbon are olefines and benzene.

Finely divided platinum and copper have no action on ethylene below 400°, but cobalt above 300° partially decomposes it into ethane, methane, and hydrogen, together with carbon, but without any acetylene. Iron above 350° has less action but decomposes a small part of the gas into ethane, hydrogen, and carbon. C. H. B.

Behaviour of Acetylene on Oxidation. By A. BASCHIERI (*Atti Real. Accad. Lincei*, 1900, [v], 9, i, 391—393).—On oxidising acetylene with fuming nitric acid (sp. gr. 1.52), the principal products are nitroform and carbon dioxide; besides these, a mixture of acids is obtained, partly crystallising from benzene in pale yellow needles melting at 145—150°. Two neutral products are also formed: (1) a small quantity of a pale yellow oil which is heavier than water, has an aromatic odour, and boils at 92° under 15 mm. pressure; (2) a solid, $C_6H_4O_3N_4$, separating from ether, alcohol, water, or light petroleum in yellowish-white needles which begin to soften at 116°, melt at 120°, and when more strongly heated give off hydrogen cyanide. T. H. P.

Action of Hydrogen Peroxide on Unsaturated Hydrocarbons. By CHARLES F. CROSS, EDWARD J. BEVAN, and TH. HEIBERG (*Ber.*, 1900, 33, 2015—2018).—On passing acetylene into dilute aqueous hydrogen peroxide containing a small quantity of ferrous sulphate, the main product of the reaction is acetic acid, small proportions of alcohol and acetaldehyde being also formed.

On heating benzene with a dilute solution of hydrogen peroxide (2 mols.) and a small quantity of crystallised ferrous sulphate in a reflux apparatus at 45°, the products obtained were phenol, catechol, and a trace of quinol, together with a brown, amorphous product, which, on heating with potassium hydroxide at 200°, yielded mainly catechol, and also readily formed a crystalline bromo-derivative. T. H. P.

Nitrotri-iodoethylene and Dinitrodi-iodoethylene. By HEINRICH BILTZ and ERICH KEDESZY (*Ber.*, 1900, 33, 2190—2196).—The compound described by Nef (*Abstr.*, 1898, i, 114) as tri-iodovinyl

nitrate is identical with nitrotri-iodoethylene (Biltz, Abstr., 1897, i, 389). It melts at 107° , and, contrary to Nef's statement, is quite stable in the dark or in diffused daylight; it is not immediately hydrolysed by alkalis, and when reduced in either alkaline or acid solution yields ammonia.

Dinitrodi-iodoethylene, $C_2I_2(NO_2)_2$, is obtained, together with nitrotri-iodoethylene, by the action of warm fuming nitric acid on tetraiodoethylene. It crystallises in yellow, monoclinic needles, melts at $68-69^{\circ}$, and is readily soluble in most organic solvents, with the exception of light petroleum. It is readily decomposed by potassium hydroxide solution, and even in the dark evolves iodine.

These iodo-derivatives correspond with the bromo-compounds described by Scholl and Brenneisen (Abstr., 1898, i, 345). J. J. S.

Influence of Hydrobromic Acid on the Rate of Action of Bromine or Trimethylene. By GABRIEL GUSTAVSON (*Compt. rend.*, 1900, 131, 273—274).—Dry bromine acts but slowly on trimethylene, but in presence of a small quantity of hydrobromic acid the hydrocarbon is rapidly absorbed, with considerable development of heat. After some time, however, this effect disappears, although the quantity of hydrobromic acid present remains the same. The active agents in promoting the absorption are compounds of bromine and hydrobromic acid of the type described by Berthelot; if 12 grams of bromine are agitated with 0.3 c.c. of hydrobromic acid of the composition $HBr, 5H_2O$, the liquid separates into two layers, the upper of which contains the compounds referred to, and, if separated from the lower layer, absorbs trimethylene rapidly. The function of the hydrobromic acid seems to be similar to that of aluminium chloride or bromide. Its presence has no effect on the proportion of propylene bromide amongst the products of the bromination of trimethylene. C. H. B.

Solutions of Ferric Chloride in Organic Solvents. By WILLIAM ECHSNER DE CONINCK (*Compt. rend.*, 1900, 131, 275—276).—When a dilute solution of ferric chloride in alcohol of 95° is exposed to sunlight, small quantities of aldehyde are formed, and, if the liquid is filtered repeatedly through animal charcoal, the whole of the iron is removed, whilst a considerable quantity of chlorine remains in solution. The small quantity of water in the alcohol seems to have considerable influence in decomposing the iron salt. A dilute solution of ferric chloride in methyl alcohol free from water is also rapidly decomposed in a similar manner when filtered through animal charcoal. Ethyl acetate and acetone behave differently; the animal charcoal removes the iron salt as a whole, and hence it would seem that it is not decomposed in solution. C. H. B.

Action of Potassium Hydroxide on Epichlorhydrin in the Presence of Alcohols. II. By V. ZUNINO (*Atti Real. Accad. Lincei*, 1900, [v], 9, i, 309—311. Compare Abstr., 1899, i, 410).—By the method previously given (*loc. cit.*), the following ethers of glycerol have been prepared. The *diisopropyl* ether, $C_9H_{20}O_3$, a pale greenish-yellow, odourless liquid, boiling at $112-113^{\circ}$, and having a sp. gr. 0.917 at 15° ; the *ditert.butyl* ether, $C_{11}H_{24}O_3$, a colourless liquid with

an irritating odour, boiling at 209—210°, and having a sp. gr. 0.921 at 15°; a *dicapryl* ether, $C_{15}H_{32}O_2$, a pale yellow liquid with an irritating odour, boiling at 180° and having a sp. gr. 0.987 at 15°; *dioctyl* ether, $C_{19}H_{40}O_2$, a pale yellow liquid with a very disagreeable odour, boiling at 224° and having a sp. gr. 0.990 at 15°; *dibenzyl* ether, $C_{17}H_{20}O_2$, an opalescent liquid having a faint aromatic odour, boiling at 157—158°, and having a sp. gr. 0.918 at 15°. T. H. P.

Action of Bromine and Carbon Disulphide on Sodium Methylene Compounds. By G. WENZEL (*Ber.*, 1900, 33, 2041—2043).—On adding a slight excess of bromine, dissolved in carbon disulphide, to a suspension of freshly prepared dry ethyl sodiomalonate in this medium, a *compound* of the composition $C_{16}H_{22}O_8S_3$, and the probable constitution $S[CS \cdot CH(CO_2Et)_2]_2$, is obtained, which separates from alcohol in almost colourless needles, melts at 139°, and is insoluble in sodium hydroxide. It dissolves in concentrated sulphuric acid, and, after many hours standing, water precipitates from the solution a colourless acid which dissolves readily in cold sodium hydroxide.

Under similar conditions, ethyl sodiocyanoacetate gives rise to a *compound* of the composition $C_{12}H_{12}O_4N_2S_3$, which crystallises from alcohol, toluene, or glacial acetic acid in yellow needles melting at 225°.

With the sodium derivatives of acetylacetone, ethyl acetoacetate, and ethyl phenylacetate, negative results were obtained.

T. H. P.

Haloid Hydroxy-acids. By PETR. G. MELIKOFF (*J. pr. Chem.*, 1900, [ii], 61, 554—560).—Chlorohydracrylic acid, when distilled with sulphuric acid, yields α -chloroacrylic acid; its *ethyl* ester boils at 207—208°. Hypobromous acid reacts with crotonic acid (compare *Abstr.*, 1883, 311), to form principally α -bromo- β -hydroxybutyric acid, which crystallises in monoclinic prisms melting at 86—87° and, when distilled with sulphuric acid, yields α -bromocrotonic acid; β -bromo- α -hydroxybutyric acid, which is also formed in small quantity, crystallises in rhombic prisms melting at 96—97°, yields β -bromocrotonic acid when distilled with sulphuric acid, and forms a *sodium* salt, which, when heated, yields propaldehyde. The paper concludes with a summary of the facts known about the addition of hypochlorous or hypobromous acid to unsaturated acids of the type of crotonic acid; this reaction appears to follow no special rule, but stereoisomeric unsaturated acids yield corresponding stereoisomeric haloid hydroxy-acids.

R. H. P.

Synthesis of Sorbic Acid. By OSCAR DOEBNER (*Ber.*, 1900, 33, 2140—2142).—It has not been found possible to synthesise sorbic acid, $CHMe:CH:CH:CH:CO_2H$, from crotonaldehyde and acetic acid by the Perkin reaction, but a good yield of the acid is obtained when crotonaldehyde is heated with malonic acid and pyridine. C. F. B.

Oxidation of Citric Acid and Citrates with Potassium Permanganate or with Iron. By LUIGI SABBATANI (*Atti Accad. Sci. Torino*, 1900, 35, 678—684).—The formation of acetonedicarb-

oxylic acid by the oxidation of citric acid with cold permanganate was discovered by the author and Bergesio (*Abstr.*, 1899, i, 733) prior to the publication of Denigès' results (this vol., i, 204). If the oxidation is carried out in hot solutions, acetone is obtained. The neutral salts of citric acid yield oxalic acid when treated with permanganate whilst the acid salts give both acetone and oxalic acid. The best yield of acetone is obtained by adding the permanganate drop by drop to a boiling solution of the acid; if excess is used, the acid or its salts are completely decomposed into water and carbon dioxide but with smaller quantities, the amount of acetone or oxalic acid formed is proportional, within limits, to the quantity of permanganate used.

Acetone is formed when Kämmerer's citrate of iron, $\text{FeC}_6\text{H}_6\text{O}_7 \cdot \text{H}_2\text{O}$ (*Abstr.*, 1874, 252), or a solution of citric acid containing either iron filings or a small quantity of ferric chloride, is exposed to the air.

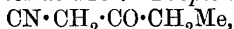
T. H. P.

Reactions of Paraformaldehyde. By LOUIS HENRY (*Chem. Centr.*, 1900, i, 1122—1123; from *Bull. Acad. roy. Belg.*, 1900, 48—56).—When phosphorus pentachloride acts on paraformaldehyde, $(\text{HCHO})_n$, at the ordinary temperature, heat is evolved and dichloromethane formed, although in rather small quantity. A good yield of dibromomethane may be obtained, however, by the action of phosphorus pentabromide or of a mixture of phosphorus trichloride (1 mol.) and bromine (1 mol.) on paraformaldehyde; in both cases, the action is rather violent. Chloromethyl acetate, $\text{MeCO}_2 \cdot \text{CH}_2\text{Cl}$, is best prepared by heating acetyl chloride (1 mol.) and paraformaldehyde (1 mol.) at 100° ; it may also be obtained by the action of chlorine, or, better, of sulphuryl chloride, on methyl acetate in sunlight. Hydrogen chloride does not act on paraformaldehyde, but by the action of hydrogen bromide, dibromomethyl ether, $(\text{CH}_2\text{Br})_2\text{O}$, is formed. Acetyl bromide also acts much more readily on paraformaldehyde than acetyl chloride. The product of the former reaction, *bromomethyl acetate*, is a pungent, colourless liquid, boils at 130° under 746 mm. and at 70° under 70 mm. pressure, has a sp. gr. 1.6560 at 12° , and does not dissolve in water but is gradually decomposed by it, forming hydrogen bromide, acetic acid, and paraformaldehyde. The formation of additive products of paraformaldehyde with acid chlorides and bromides is apparently a general reaction for the preparation of simple halogen substituted derivatives of methyl esters.

E. W. W.

Methyl Ethyl Ketone. By LOUIS HENRY (*Chem. Centr.*, 1900, i, 1123; from *Bull. Acad. roy. Belg.*, 1900, 57—63).—By the action of chlorine, or sulphuryl chloride, on methyl ethyl ketone in sunlight, *chloromethyl ethyl ketone*, $\text{CH}_3\text{Cl} \cdot \text{COEt}$, and *methyl β -chloroethyl ketone*, $\text{COMe} \cdot \text{CHClMe}$, are formed. The former boils at 124 — 125° , and, by the action of nitric acid, yields chloroacetic acid, whilst the latter boils at 114 — 115° , and, on oxidation, forms α -chloropropionic acid. Bromine also attacks the ketone energetically, forming two *monobromo-derivatives*, each of which boils about 20° higher than the corresponding chloro-derivative. By the action of an alcoholic solution of potassium acetate on the chloro-ketones, the *acetates*

$\text{CH}_2\text{Ac}\cdot\text{CO}\cdot\text{CH}_2\text{Me}$ and $\text{COMe}\cdot\text{CHMeAc}$ are formed respectively; the former boils at 176° , and the latter at 164° . The corresponding keto-alcohols, *propionyl carbinol*, $\text{CH}_2(\text{OH})\cdot\text{CO}\cdot\text{CH}_2\text{Me}$, and *methylacetyl carbinol*, $\text{COMe}\cdot\text{CHMe}\cdot\text{OH}$, prepared by hydrolysing the acetates, are colourless liquids, heavier than water and soluble in it; the former boils at 160° and the latter at 148° . *Propionylacetonitrile*,



prepared by the action of a cold concentrated aqueous solution of potassium cyanide on the corresponding chloro-derivative, boils at $164\text{--}165^\circ$. α -*Acetylpropionitrile*, $\text{CN}\cdot\text{CHMe}\cdot\text{COMe}$, similarly obtained, boils at $145\text{--}146^\circ$ and is insoluble in water. In both these nitriles the hydrogen atom combined with the carbon to which the cyanogen group is attached may be replaced by metals. By the action of methyl iodide on the sodium compound of α -acetylpropionitrile, *dimethylacetylacetonitrile*, $\text{CN}\cdot\text{CMe}_2\cdot\text{COMe}$, boiling at $163\text{--}164^\circ$, is formed. α -*Acetyl- α -chloropropionitrile*, prepared by the action of sulphuryl chloride on the ketonitrile, or on its sodium compound, is a faintly yellow liquid of an extremely pungent odour, boils at 95° under 45 mm. pressure and, when treated with potassium cyanide, yields *methylacetylmalonitrile*, $\text{CMe}(\text{CN})_2\cdot\text{COMe}$, which boils at 122° under 30 mm. pressure. All the cyano-derivatives are easily decomposed by acids. The ketonitriles withstand the action of aqueous solutions of alkalis much better than the isomeric butyryl and isobutyryl cyanides

E. W. W.

Condensation of Nitromalonic Aldehyde with Ketones and Ketonic Acids. By HENRY B. HILL, CHARLES A. SOCH, and GEORGE OENSLAGER (*Amer. Chem. J.*, 1900, 24, 1—15. Compare Abstr., 1899, i, 788).—The condensation products of sodium nitromalonaldehyde with methyl ethyl ketone, dibenzyl ketone, ethyl acetoacetate, lævulic acid, and acetonedicarboxylic acid have been studied. The condensation takes place most readily in cold aqueous solution in the presence of a slight excess of sodium hydroxide, but with dibenzyl ketone it is advisable to employ an alcoholic solution.

With methyl ethyl ketone, the product is 4-nitro-*o*-cresol.

2:6-Diphenyl-4-nitrophenol, obtained from dibenzyl ketone, crystallises from hot alcohol in obliquely truncated prisms melting at $135\text{--}136^\circ$. The potassium derivative, $\text{C}_{18}\text{H}_{12}\text{O}_3\text{NK}\cdot\text{H}_2\text{O}$, crystallises in short, yellow needles sparingly soluble in cold water, and when dehydrated at 100° becomes a brilliant red; the methyl ether forms oblique prisms melting at $152\text{--}153^\circ$ (corr.). The corresponding aminophenol melts at $149\text{--}150^\circ$ (corr.), the quinone at $135\text{--}136^\circ$ (corr.), and the quinol at $179\text{--}180^\circ$ (corr.) (compare Borsche, this vol., i, 25).

m-Nitrosalicylic acid is obtained from ethyl acetoacetate.

With lævulic acid, 5-nitro-2-hydroxyphenylacetic acid is formed; it crystallises from water in long, slender prisms, melts, when rapidly heated, at $160\text{--}162^\circ$, but if kept at $148\text{--}149^\circ$ for 15 minutes it also melts, owing to its conversion into a lactone, $\text{C}_8\text{H}_5\text{O}_4\text{N}$, which sublimes in an atmosphere of carbon dioxide under a pressure of 50—60 mm., as large, colourless, transparent prisms, melts at $187\text{--}188^\circ$ (corr.),

and dissolves readily in hot benzene, acetone, or acetic acid. The *ethyl* ester crystallises from alcohol in flat prisms melting at 154—155° (corr.).

2 : 6-Dicarboxy-4-nitrophenol, $\text{OH} \cdot \text{C}_6\text{H}_2(\text{CO}_2\text{H})_2 \cdot \text{NO}_2$, obtained from acetonedicarboxylic acid, crystallises from hot water in finely felted, colourless needles containing $1\text{H}_2\text{O}$. The anhydrous acid melts at 213—214° (corr.), and the hydrated form some 20° lower. The various sodium salts and the silver salt, $\text{C}_8\text{H}_3\text{O}_7\text{Na}_2$, have been prepared.

J. J. S.

An Optically Inactive Pentose in Urine. By CARL NEUBERG (*Ber.*, 1900, 33, 2243—2254. Compare Salkowski, *Abstr.*, 1893, ii, 100; 1899, ii, 679).—Salkowski's pentose has been purified by conversion into the diphenylhydrazone, and the hydrolysis of this hydrazone by Ruff and Ollendorff's method (this vol., i, 77). From a study of the derivatives, it would appear that this pentose is *r*-arabinose, and it is thus the first racemic sugar which has been found to occur naturally.

r-Arabinosediphenylhydrazone, $\text{C}_{17}\text{H}_{20}\text{O}_4\text{N}_4$, crystallises from aqueous pyridine in colourless needles, sinters at 203°, melts at 206°, and is sparingly soluble in most solvents. When decomposed with formaldehyde solution, it yields a sugar identical with *r*-arabinose; the osazone melts at 166—168°, the *p*-bromophenylhydrazone at 160°, the corresponding osazone, $\text{C}_{17}\text{H}_{18}\text{O}_3\text{N}_4\text{Br}_2$, at 200—202° (compare this vol., i, 139), the phenylbenzylhydrazone, $\text{C}_{18}\text{H}_{22}\text{O}_4\text{N}_2$, at 185°, whereas the corresponding hydrazone of *l*-arabinose melts at 170° (*Abstr.*, 1897, i, 41), and of *d*-arabinose at 174° (this vol., i, 77); the phenylmethylhydrazone crystallises from alcohol in glistening needles melting at 173°. The sugar readily reacts with amyl mercaptan, yielding *r*-arabinose-amylycercaptal, which crystallises from 10 per cent. alcohol in glistening, felted needles melting at 125—130°.

The following derivatives of *l*-arabinose have been prepared:—*l*-Arabinoseamylmercaptal (compare Fischer, *Abstr.*, 1894, i, 270) melts at 132—134°, and 0.2 gram dissolved in 10 c.c. of hot absolute alcohol gives, in a decimetre tube, a rotation $+0^\circ55'$. *l*-Arabinosediphenylhydrazone melts at 218°, and 0.2 gram dissolved in 4 c.c. of pyridine and 6 c.c. of absolute alcohol gives a rotation of $+0^\circ42'$. J. J. S.

Conversion of Gulonic Acid into Xylose and Galactose. By EMIL FISCHER and OTTO RUFF (*Ber.*, 1900, 33, 2142—2147).—The calcium salt of *d*-gulonic acid, which is obtained by reduction of saccharic acid, is oxidised by hydrogen peroxide, in the presence of a little ferric acetate and in slightly warm solution, to *d*-xylose, which melts at 141.5—143° (corr.), has a specific rotation $[\alpha]_D -18.6^\circ$ at 20°, and is oxidised by bromine to an acid of which a double salt, $(\text{C}_5\text{H}_9\text{O}_6)_2\text{Cd} \cdot \text{CdBr}_2 \cdot 2\text{H}_2\text{O}$, was prepared, identical in appearance and composition with the corresponding derivative of *l*-xylonic acid. Xylose can be converted into the isomeric sugar lyxose (compare *Abstr.*, 1896, i, 348). *d*-Lyxose is now found to yield *d*-galactonic acid, along with some talonic acid, when it is treated with hydrocyanic acid. Since saccharic acid is prepared from dextrose, which can be synthesised, and galactonic acid is connected with galactose and

dulcitol, the synthesis of a member of the dulcitol group, hitherto not accomplished, has now been effected.

l-Saccharic acid has actually been synthesised, but owing to its costliness the complete series of transformations was not carried out in this case. *l*-Gulonic acid was, however, oxidised with hydrogen peroxide, and the product was found to be identical with natural xylose (*l*-xylose). By mixing this with *d*-xylose in equal proportion and crystallising the mixture from alcohol, inactive *dl*-xylose was obtained; this melts at 129–131°, and forms a phenylosazone identical with that already obtained from xylitol (Abstr., 1894, i, 566).

C. F. B.

Oxidation Product of Glycogen with Bromine. By W. NIEBEL (*Zeit. physiol. Chem.*, 1900, 29, 482–485).—Chittenden (*Annalen*, 1876, 182, 206) stated that, by the oxidation of glycogen with bromine, he obtained a monobasic acid, $C_6H_{12}O_7$, to which the name glycogenic acid was given. In the present research, Chittenden's method with some slight modifications was found to lead, with glycogen as with other carbohydrates, to the formation of gluconic acid. The common disease of horses, hæmoglobinæmia, is believed to be due to the production of this or a higher oxidation product from the glycogen of the muscles, passing into the blood; the flesh of the horse is well known to be extremely rich in glycogen.

W. D. H.

Sugar obtained by the Hydrolysis of Strophanthin. IV. By FRANZ FEIST (*Ber.*, 1900, 33, 2091–2097).—Methylstrophanthobioside, $C_{12}H_{21}O_9 \cdot OMe$, the sugar obtained by the hydrolysis of strophanthin (Abstr., 1898, i, 329; this vol., i, 555), forms a colourless, crystalline powder melting at 207°. When hydrolysed, it yields methyl alcohol, *d*-mannose and *d*-rhamnose, and is the first crystalline methyl ether of a saccharobiose (from the combination of a hexose and a methylpentose) which has been obtained by the hydrolysis of a glucoside. R. H. P.

Oxycelluloses and the Molecular Weight of Cellulose. By A. NASTUKOFF (*Ber.*, 1900, 33, 2237–2243).—The author has obtained two oxycelluloses from cellulose, the one by the aid of bleaching powder solution and the second by means of a 1 per cent. neutral permanganate solution. Both were purified by solution in 10 per cent. sodium hydroxide solution and subsequent precipitation with hydrochloric acid, and both possess the ordinary reducing properties of oxycelluloses, yield compounds with phenylhydrazine, and turn yellow when warmed with sodium hydroxide. When the second oxycellulose is boiled with a 5 per cent. sodium hydroxide solution, 70 per cent. of it is converted into a white powder which no longer has reducing properties but possesses the same percentage composition as the original substance (compare Faber and Tollens, Abstr., 1899, ii, 854). The molecular weights of triacetylcellulose and triacetyl-oxycellulose have been determined in nitrobenzene solution by the boiling point method. The results point to a molecule $40C_6H_{10}O_5$ for cellulose and indicate that the formation of oxycellulose by the aid of bleaching powder is merely a process of oxidation and not of hydrolysis.

J. J. S.

Cellulose Nitrates. By A. LUCK and CHARLES F. CROSS (*J. Soc. Chem. Ind.*, 1900, **19**, 642—644).—The instability of the cellulose nitrates is not merely due to incomplete removal of all traces of the nitrating acid, as subsequent extraction with water, alcohol, ether, or benzene does not render them stable. Treatment with 50 per cent. aqueous acetone, however, renders the substance much more stable than when boiled and washed in water in the usual way, whilst with 90—93 per cent. acetone structural disintegration of the nitrate occurs, and the substance can be obtained in the form of a hard, dense powder. The impurities which lower the stability of the nitrate are present in the acetone filtrate, and seem to have acid characters, as they yield insoluble lead salts (PbO , 60—63, and N , 3.5 per cent.); their baneful influence may be eliminated by treating the nitrate with lead or zinc oxide. The purest cellulose nitrate, however, slowly decomposes with formation of unstable acid products when boiled for some time in water. J. J. S.

Preparation and Properties of Diastase-Achroodextrin III. By EUGEN PRIOR and D. WIEGMANN (*Zeit. angew. Chem.*, 1900, 464—469. Compare Abstr., 1897, i, 312).—Achroodextrin III, identical with Ling and Baker's "malto-dextrin- β " (*Trans.*, 1897, **71**, 508), is almost insoluble in 90 per cent. alcohol. It has the specific rotation $[\alpha]_D$ 171.1, and reducing power R 42.5. Its mol. weight, determined by the cryoscopic method, is 642, corresponding more closely with the formula $2(\text{C}_{12}\text{H}_{20}\text{O}_{10})$ than with that proposed by Ling and Baker, namely, $2(\text{C}_{12}\text{H}_{20}\text{O}_{10})\cdot\text{H}_2\text{O}$, which is, however, the more probable expression. Phenylhydrazine gives no trace of crystalline osazone. Achroodextrin III is completely fermented by Logos yeast, partially by Saaz and Froberg yeasts, and not at all by *Saccharomyces apiculatus*; the fermentation appears to be direct, as no sugar can be detected if the yeast used has been freed from sugar before digestion. By the action of diastase, achroodextrin III is converted to *achroodextrin* IV, which is further hydrolysed into maltose (Ling and Baker, *loc. cit.*).

From the original starch-conversion, erythro-dextrin and achroodextrin II were also prepared in a pure state. The latter, after prolonged contact, is fermented to the extent of 3 per cent. by Saaz yeast, 14 per cent. by Froberg, and 75.4 per cent. by Logos yeast.

The low diffusibility of dextrans is offered as an explanation of the difficulty experienced in fermenting them. R. L. J.

Ammonio-oxycobalt Thiocyanates. By E. MASCETTI (*Zeit. anorg. Chem.*, 1900, **24**, 188—190).—The blackish-green intermediate compounds obtained in the preparation of ammonio-cobalt thiocyanates (Miolati, this vol., i, 381) are oxycobaltamine thiocyanates. The salt, $\text{Co}_2\text{O}_2(\text{NH}_3)_{10}(\text{SCN})_4$, obtained by passing a current of air through a strongly ammoniacal solution of cobalt sulphate or thiocyanate and ammonium thiocyanate, crystallises in large, well-formed black crystals, and decomposes on exposure to air, changing to red and evolving ammonia. The salt $\text{Co}_2\text{O}_2(\text{NH}_3)_{10}(\text{SCN})_2(\text{NO}_3)_2$, obtained in the same manner from cobalt nitrate, separates in dirty,

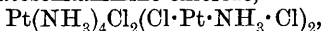
olive-green crystals, and decomposes more readily than the preceding compound.
E. C. R.

Preparation of Zinc Ethyl By ARTHUR LACHMAN (*Amer. Chem. J.*, 1900, 24, 31—39. Compare Abstr., 1897, i, 461).—The author describes in fuller detail the method already given. A method is also given for the recovery of iodine from the residues obtained in the preparation of zinc ethyl.
J. J. S.

Pallado-oxalic Acid and Pallado-oxalates. By H. LOISELEUR (*Compt. rend.*, 1900, 131, 262—264. Compare Vèzes, Abstr., 1899, i, 672).—*Silver pallado-oxalate*, $\text{Ag}_2\text{Pd}(\text{C}_2\text{O}_4)_2 \cdot 3\text{H}_2\text{O}$, is almost insoluble in cold water, but crystallises from hot water in golden-yellow needles. When exposed to light or when the solution is boiled, the salt is partially reduced. The *acid*, although somewhat unstable, can be obtained in bulky, brownish-yellow needles of the composition $\text{H}_2\text{Pd}(\text{C}_2\text{O}_4)_2 \cdot 6\text{H}_2\text{O}$; when exposed to light, or when its solution is boiled, it decomposes into palladium, oxalic acid, and carbon dioxide. The *sodium* salt, $\text{Na}_2\text{Pd}(\text{C}_2\text{O}_4)_2 \cdot 2\text{H}_2\text{O}$, forms brownish-yellow, efflorescent needles. The *barium* salt crystallises from hot water, with $3\text{H}_2\text{O}$, in small yellow needles.
C. H. B.

Constitution of Platinum Bases. By SOFUS M. JØRGENSEN (*Zeit. anorg. Chem.*, 1900, 24, 153—182).—Platodiammine platosemiethylene chloride, $\text{Pt}(\text{NH}_3)_4\text{Cl}_2(\text{Cl} \cdot \text{Pt} \cdot \text{C}_2\text{H}_4\text{Cl})_2$, is obtained by warming sodium platinichloride with absolute alcohol until a sample of the mixture is not precipitated by concentrated ammonium chloride; the filtrate, which contains the acid corresponding to Zeise's salt, is diluted with water and a solution of platodiammine chloride added when the platodiammine salt is precipitated. It crystallises in fine yellow rhombohedra or monoclinic tablets, is very heavy, very sparingly soluble in cold water; when boiled with water or very dilute hydrochloric acid it is decomposed and yields platodiammine chloride and platinum. It can be recrystallised from hot normal hydrochloric acid in the dark; and on exposure to light is gradually converted into Magnus' salt, hydrogen platinochloride, and ethylene. *Potassium platosemiethylene chloride*, $\text{KCl}_2\text{Pt} \cdot \text{C}_2\text{H}_4 \cdot \text{Cl} \cdot \text{H}_2\text{O}$, crystallises in hemimorphic, monoclinic forms: $[a:b:c = 0.6374:1:0.8637; \beta = 95^\circ 29' 5'']$; sp. gr. = 2.88; the *ammonium* salt is isomorphous with it $[a:b:c = 0.6456:1:0.8690; \beta = 95^\circ 29']$; sp. gr. 2.68.

Platodiammine platosemiammine chloride,



described by Cossa (Abstr., 1896, ii, 251), is most easily prepared by warming platosemidiammine chloride with normal hydrochloric acid for 30—36 hours on the water-bath, and after cooling, precipitating with an aqueous solution of platodiammine chloride; it crystallises in lustrous, yellow leaflets. The potassium salt, $\text{KCl}_2\text{Pt} \cdot \text{NH}_3 \cdot \text{Cl} \cdot \text{H}_2\text{O}$, crystallises in the rhombic system $[a:b:c = 0.6310:1:0.8231]$; the *ammonium* salt, $\text{NH}_4\text{Cl}_2\text{Pt} \cdot \text{NH}_3 \cdot \text{Cl} \cdot \text{H}_2\text{O}$, forms large, lustrous, orange red prisms, and when heated with dilute ammonium chloride is converted into platosemidiammine chloride.

Potassium platosemiethylene chloride and potassium platosemiammine

chloride, when treated with silver nitrate, are converted into the corresponding silver salts, contrary to Blomstrand's and Cossa's statements.

E. C. R.

Action of Allyl alcohol on Potassium Platinochloride. By EINAR BILLMANN (*Ber.*, 1900, 33, 2196—2201. Compare Jörgensen, preceding abstract).—Allyl alcohol reacts with a warm aqueous solution of potassium platinochloride according to the equation $C_3H_5 \cdot OH + K_2PtCl_4 = Cl(C_3H_5 \cdot OH)PtCl \cdot ClK + KCl$, but the *potassium platosemiallyl alcohol chloride* has not been obtained in a pure state. When the product is treated with platodiammine chloride, *platodiammineplatosemiallyl alcohol chloride*, $Pt[(NH_3)_2Cl \cdot ClPt(C_3H_5 \cdot OH)Cl]_2$, is obtained in the form of minute, felted, yellow needles; it is moderately soluble in cold water, but decomposes when the solution is boiled. Magnus's salt is obtained when it is boiled with hydrochloric acid, or when ammonia is added to the products of the action of allyl alcohol on potassium platinochloride, the mixture then acidified with hydrochloric acid and treated with potassium platinochloride, a dark red compound being also formed in the latter case. Alkaloidal salts give precipitates with the solution of potassium platosemiallyl alcohol chloride; the *cinchonine* compound has the composition $C_{19}H_{22}ON_2[HCl_2Pt(C_3H_5 \cdot OH)Cl]_2$.

J. J. S.

Osmyloxalates. By L. WINTREBERT (*Compt. rend.*, 1900, 131, 264—267).—Potassium osmyloxalate, $K_2OsO_2(C_2O_4)_2 \cdot 2H_2O$, already obtained by Vèzes by the action of oxalic acid on a solution of osmium peroxide in potassium hydroxide, can also be prepared by adding a slight excess of oxalic acid to a warm concentrated alkaline solution of potassium osmate, and crystallises in brown needles. The sodium salt is obtained in a similar manner, and forms brown needles much more soluble in cold water. Both salts are unstable in solution and gradually yield a black precipitate of osmic acid, but this change is prevented by the presence of a small quantity of oxalic acid or an alkali oxalate. The corresponding silver salt forms greenish-brown crystals and is unstable.

When potassium osmyloxalate is boiled with hydrochloric acid, it yields potassium osmichloride, chlorine, oxalic acid, and water, and hydrobromic acid yields similar results. The osmyloxalates, therefore, seem to be analogous to the osmysulphites and the salts of osmyl ammonium.

C. H. B.

Action of a Mixture of Benzene Vapour and Hydrogen on Platinum and Palladium Black. By GEORG LUNGE and J. AKUNOFF (*Zeit. anorg. Chem.*, 1900, 24, 191—202. Compare Harbeck and Lunge, *Abstr.*, 1898, ii, 193).—A mixture of hydrogen with 5 to 8 per cent. of benzene vapour, when passed over platinum black 25 times at the ordinary temperature, undergoes contraction corresponding with the complete conversion of the benzene into hexahydrobenzene; a complete conversion is obtained at 100° by passing the gases only three times over the platinum black. Palladium black acts in a similar manner, but more readily; the product at the ordinary temperature is, however, tetrahydrobenzene. Both platinum and palladium

black become inactive after large quantities of the gas have been passed over them, and are only rendered active again by heating in a current of hydrogen. Owing to the proximity of the boiling points, the authors were unable to separate the tetra- and hexa-hydrobenzene from the excess of benzene. E. C. R.

The Number of Isomeric Naphthalene Derivatives. By HUGO KAUFFMANN (*Ber.*, 1900, **33**, 2131—2134. Compare Rey, this vol., i, 482, and Fulda, quoted by Noetting, *Mon. sci.*, 1894, [iv], **81**, 178).—A formula is given by means of which the number of isomeric naphthalene derivatives may be calculated. C. F. B.

Crystalline Form of Tolane. By GIOVANNI BOERIS (*Atti Real. Accad. Lincei*, 1900, [v], **9**, i, 382—383).—Tolane crystallises in the monoclinic system [$a:b:c = 2.21081:1:1.35990$; $\beta = 64^\circ 59'$]. The crystals show great similarity to those of stilbene, dibenzyl, and azobenzene (Abstr., 1899, ii, 731 and 732). T. H. P.

Reactions of Aniline and of Hydroxylamine with Hydroxy- and Unsaturated Compounds. By ALFRED TINGLE (*Amer. Chem. J.*, 1900, **24**, 45—59).—With the object of ascertaining whether β -ketonic esters react in the ketonic or enolic form when undergoing condensation with amino-compounds, the reaction between aniline or hydroxylamine and different hydroxy- and unsaturated esters has been studied, but so far no generalisations can be drawn.

When aniline and ethyl tartrate are boiled together for 2 hours, the products are tartranilide and *ethyl phenyltartrate*, $\text{CO}_2\text{Et} \cdot \text{CH}(\text{OH}) \cdot \text{CH}(\text{OH}) \cdot \text{CO} \cdot \text{NHPh}$; the latter is soluble in water, crystallises in small, colourless plates, and melts at $152\text{--}153^\circ$.

Ethyl cinnamate and hydroxylamine yield phenylisooxazole (Abstr., 1891, 468) and an uncrystallisable oil.

Jeanrenaud's work on the action of methyl salicylate on hydroxylamine (Abstr., 1889, 870) has been repeated and his results confirmed; when, however, a smaller amount of alkali is employed, the product is salicylic acid, and not salicylhydroxamic acid.

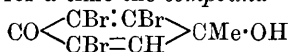
Methyl salicylate and aniline, when perfectly dry, yield phenol and methylaniline; when the reagents are not quite dry, salicylanilide is also formed.

No reaction occurs between ethyl tartrate and hydroxylamine, ethyl cinnamate and aniline, potassium cinnamate and hydroxylamine, or sodium salicylate and aniline.

Aniline appears to react with *o*- or *p*-nitrophenol, but no well defined products have been obtained. J. J. S.

Removal or Substitution of Sulphonic Groups in Naphthalene Derivatives by Nascent Chlorine. By WILHELM VAUBEL (*Zeit. angew. Chem.*, 1900, 686—687).—Nascent bromine fails to displace sulphonic groups from naphthol- and naphthylamine-sulphonic acids. Nascent chlorine displaces sulphonic groups when they occur in *o*- and *p*-positions, except in α -naphthylamine-4:8- and -2:7-disulphonic acids and α -naphthol-4:8-disulphonic acid, but does not affect them when in the *m*-position or when heteronuclear. R. L. J.

Action of Nitrous Acid on Bromo- and Chloro-derivatives of Phenols. By THEODOR ZINCKE (*J. pr. Chem.*, 1900, [ii], 61, 561—567).—Bromo- and chloro-phenols, when treated with nitrous acid, are always converted into nitrophenols, in most cases the halogen, but sometimes a hydrogen atom, being replaced by the nitro-group. In this way, mono- and di-bromo-*p*-cresol yield the same 3-bromo-5-nitro-*p*-cresol (m. p. 68°), tribromo-*p*-cresol yields a dibromonitro-*p*-cresol (m. p. 124°), and tetrabromo-*p*-cresol yields a tribromonitro-*p*-cresol (m. p. 160°); similarly, 5-bromo-*o*-cresol and 3:5-dibromo-*o*-cresol yield 3-nitro-5-bromo-*o*-cresol (m. p. 88°), tribromo-*o*-cresol yields a dibromonitro-*o*-cresol (m. p. 141°), and tetrabromo-*o*-cresol yields tribromo-3-nitro-*o*-cresol (m. p. 156°). The action of nitrous acid on bromo-derivatives of *m*-cresol is not quite clear; nitro-derivatives are produced, but molecular transformation appears also to take place. Some of the above derivatives can also be prepared by means of nitric acid, while in some cases, for example, dichloro- and dibromo-*p*-cresol, by the action of nitric acid, the unstable nitroketones are obtained; on the other hand, chloro- and bromo-*p*-cresol, when treated with nitric acid, yield nitrated oxyketones. Tribromo-*p*-cresol, when treated with nitric acid in acetic acid solution, yields the above-mentioned dibromonitro-*p*-cresol if immediately precipitated by water, but if the solution is left for a time the compound



is obtained. This forms clear, tabular crystals, melts at 128°, gives a yellow solution in sodium hydroxide, yields a crystalline *acetyl* derivative melting at 127—128°, and is reconverted into tribromo-*p*-cresol on reduction. R. H. P.

Derivatives of 2-Methyl-1:3:4:5-Phentetrol. By KARL KONYA (*Monatsh.*, 1900, 21, 422—432).—3-Hydroxy-5-methoxy-2-methyl-*p*-quinone-4-monoxime, obtained when methylphloroglucinol mono-methyl ether is treated with potassium nitrite and acetic acid, forms flaky, violet crystals, which have a metallic lustre and explode at 194°. When reduced with stannous chloride, it is converted into 4-amino-3-hydroxy-5-methoxy 2-methylphenol hydrochloride; this crystallises in groups of colourless, slender needles, and yields a *tetracetyl* derivative of the base, which forms small, snow-white crystals melting at 178°. When oxidised with ferric chloride, the hydrochloride forms 3-hydroxy-5-methoxy-2-methyl-*p*-quinone, crystallising in small, flaky, yellowish crystals, which begin to sublime at 160° and melt at 186°. The corresponding *quinol* crystallises in small, slender, transparent needles, oxidises quickly when exposed to air, decomposes at 134°, and yields a *triacetyl* derivative melting at 174°. R. H. P.

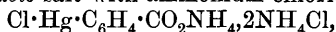
Monoalkyl Ethers of Phloroglucinol. By JOSEF HERZIG and F. AIGNER (*Monatsh.*, 1900, 21, 433—445).—Phloroglucinol mono-methyl ether (this vol., i, 290) is easily prepared by the reduction of *sym*-dinitroanisole and hydrolysis of the resulting *diaminoanisole dihydrochloride*, which forms a colourless, crystalline mass decomposing at 220°; the *tribromo*-derivative, $\text{OMe} \cdot \text{C}_6\text{Br}_3(\text{OH})_2$, crystallises in long, transparent needles melting at 123°, and forms a *diacetyl* deriva

tive which crystallises in long, white needles melting at 112—114°; the *dibenzoyl* derivative, $\text{OMe} \cdot \text{C}_6\text{H}_3(\text{OBz})_2$, forms slender, colourless needles, melts at 96°, and is easily hydrolysed; the *diacetyl* derivative, $\text{OMe} \cdot \text{C}_6\text{H}_3(\text{OAc})_2$, crystallises in long, colourless needles melting at 74°.

Phloroglucinol monoethyl ether can be prepared in a similar manner from *sym*-dinitrophenetole. R. H. P.

Organo-mercury Compounds of Benzoic Acid. By LEONE PESCI (*Atti Real. Accad. Lincei*, 1900, [v], 9, i, 255—262).—*Hydroxy-mercuribenzoic anhydride*, $\text{C}_6\text{H}_4 \begin{smallmatrix} \text{CO} \\ \diagup \text{Hg} \diagdown \end{smallmatrix} \text{O}$, is prepared by heating mercuric acetate with benzoic acid until potassium hydroxide fails to precipitate mercuric oxide, and then treating with ammonia solution to obtain ammonium hydroxymercuribenzoate; the anhydride is formed on treating the ammonium salt with acetic acid or the corresponding sodium salt with carbon dioxide. It forms microscopic mammillary crystals insoluble in the ordinary solvents, and is decomposed with difficulty by mineral acids; it does not melt when heated, but at high temperatures decomposes and deflagrates. The *acid* is very unstable, but its salts, formed on treating the anhydride with the corresponding hydroxide or carbonate, are strongly basic compounds readily decomposed by solvents yielding the anhydride of the acid and the metallic hydroxide; with acids, including carbonic acid, the anhydride is re-formed. The *ammonium*, $\text{OH} \cdot \text{Hg} \cdot \text{C}_6\text{H}_4 \cdot \text{CO}_2\text{NH}_4$, *barium*, *calcium*, *magnesium*, *isoamylamine*, and *benzylamine* salts are described.

By the action of the halogen hydracids on hydroxymercuribenzoic anhydride or on metallic hydroxymercuribenzoates, chloro-, bromo-, and iodo-mercuribenzoic acids may be obtained. They are unstable substances, and in presence of the halogen hydracids tend to decompose, forming benzoic acid and the mercury haloid salt. *Chloro-mercuribenzoic acid*, $\text{Cl} \cdot \text{Hg} \cdot \text{C}_6\text{H}_4 \cdot \text{CO}_2\text{H}$, is a colourless, microcrystalline powder moderately soluble, with partial decomposition, in boiling water or methyl or ethyl alcohol. Its *sodium* salt (with $2\frac{1}{2}\text{H}_2\text{O}$), *aniline* salt, and *double salt* with ammonium chloride,



are described.

Bromomercuribenzoic acid, $\text{Br} \cdot \text{Hg} \cdot \text{C}_6\text{H}_4 \cdot \text{CO}_2\text{H}$, separates from methyl or ethyl alcohol in needles; the *potassium*, *sodium* (with $4\text{H}_2\text{O}$), and *barium* (with $3\text{H}_2\text{O}$) salts were prepared.

Iodomercuribenzoic acid, $\text{I} \cdot \text{Hg} \cdot \text{C}_6\text{H}_4 \cdot \text{CO}_2\text{H}$, could not be obtained pure owing to the ease with which it decomposes. The *potassium*, *sodium*, and *barium* salts are described.

The author's previous work (*Abstr.*, 1894, i, 248) indicates that the mercury group in these compounds occupies the para-position relatively to the carboxyl radicle. T. H. P.

Commercial Dichlorophthalic Acid. By CARL GRAEBE (*Ber.*, 1900, 33, 2019—2023).—To purify commercial dichlorophthalic acid, which always contains the trichloro-acid, the following method is employed. By heating at 180—200°, the acid is completely converted into anhydride, which is then heated for about an hour in a reflux

apparatus with an equal weight of absolute alcohol; water is afterwards added until no further turbidity is formed, and the precipitated ethyl hydrogen dichlorophthalate washed with water, dried, and purified by crystallisation from carbon tetrachloride or a mixture of chloroform and light petroleum. By heating at 200° , this salt is converted into the anhydride of the acid, and on dissolving the latter in hot water, 3 : 6-dichlorophthalic acid (see following abstract) is obtained. It crystallises from water in well-developed, anhydrous plates, and has no definite melting point, since the formation of the anhydride begins below 100° ; the melting point of the latter is 191° (Faust gave 187°).

Ethyl hydrogen 3 : 6-dichlorophthalate, $C_{10}H_8O_4Cl_2$, obtained as just described or by hydrolysing the diethyl ester with 1 mol. of potassium hydroxide, melts with incipient decomposition at 128 — 130° , and is readily soluble in alcohol or chloroform, but only slightly so in water.

T. H. P.

3 : 6-Dichlorophthalic Acid. By CARL GRAEBE and S. GOUREVITZ (*Ber.*, 1900, **33**, 2023—2026).—The dichlorophthalic acid of commerce, when purified by the method described in the preceding abstract, proves to be the 3 : 6-dichloro-acid, as is shown by its conversion into *p*-dichlorobenzene, the intermediate steps in the transformation being dichlorophthalimide, dichloroanthranilic acid, and 2 : 5-dichloro-aniline.

Ethyl ammonium 3 : 6-dichlorophthalate, $CO_2Et \cdot C_6H_2Cl_2 \cdot CO_2NH_4$, is readily soluble in water and, to a less extent, in alcohol. The *silver* salt was prepared, and also the *diethyl* ester, which melts at 60° .

3 : 6-Dichlorophthalanil, $C_{14}H_7O_2NCl_2$, obtained by heating the anhydride of the acid with aniline, crystallises from alcohol in colourless needles melting at 191° .

3 : 6-Dichlorophthalimide, $C_8H_3O_2NCl_2$, is prepared by passing ammonia into molten dichlorophthalic anhydride, or by evaporating an ammoniacal solution of ethyl hydrogen dichlorophthalate to dryness and heating at 240 — 250° until gas ceases to be evolved; it is very soluble in hot alcohol, from which it crystallises in needles melting at 242° .

3 : 6-Dichloroanthranilic acid, $C_7H_5O_2NCl_2$, is obtained by heating an aqueous solution of dichlorophthalimide and sodium hydroxide with the calculated quantity of sodium hypobromite, and precipitating the filtered liquid with hydrochloric acid. It sublimes in colourless needles, melts at 142° , and dissolves readily in organic solvents and in hot water. It yields an unstable *hydrochloride*, but cannot be esterified by the action of hydrogen chloride and an alcohol. On treatment with sodium nitrite in alcoholic solution, the acid yields 2 : 5-dichlorobenzoic acid melting at 151 — 153° (Lellmann and Klotz gave 153.5°), whilst when heated at 230 — 240° it is resolved into carbon dioxide and 2 : 5-dichloroaniline, from which *p*-dichlorobenzene was obtained by the diazo-reaction.

T. H. P.

Formation of Esters in the Phthalic Acid Group. By CARL GRAEBE (*Ber.*, 1900, **33**, 2026—2028).—Like the tetrachloro-, tetrabromo-, and tetraiodo-phthalic acids, 3 : 6-dichlorophthalic acid forms an exception to Victor Meyer's esterification rule, and readily

yields in the cold an alkyl hydrogen salt. This is readily explained by Meyer's assumption that in such cases, under the influence of concentrated sulphuric or hydrochloric acid, an anhydride is formed which, with the alcohol, gives rise to the alkyl hydrogen derivative. Further exceptions to the above law are afforded by 3:6-dichlorobenzoylbenzoic and tetrachlorobenzoylbenzoic acids, which are almost quantitatively esterified in the cold. It is supposed that these acids assume the tautomeric form of hydroxyphthalides, which react with the alcohol thus: $C_6Cl_4 \left\langle \begin{array}{c} CPh(OH) \\ \text{---CO---} \end{array} \right\rangle O + Et \cdot OH = CO_2Et \cdot C_6Cl_4 \cdot CPh(OH)_2$; the additive compound then loses water, yielding the ethyl ester of the corresponding chlorinated benzoylbenzoic acid. T. H. P.

Salol. By GEORG COHN (*J. pr. Chem.*, 1900, [ii], 61, 544—553).—Salol, when heated on a water-bath with an excess of sulphuric acid, yields a mixture of phenylsulphonic and sulphosalicylic acids. Sodium sulphosalicylate, when treated with phenol and phosphorus oxychloride, yields *diphenyl sulphosalicylate*, $CO_2Ph \cdot C_6H_3(OH) \cdot SO_3Ph$, which crystallises in small needles, melts at 172—173°, and gives a brown coloration with a solution of ferric chloride. *β-Dinaphthyl sulphosalicylate*, a white powder, and *diguaiacyl sulphosalicylate*, which crystallises in needles melting at 112—113°, are described.

Salol condenses with primary or secondary amines, phenol being eliminated; *salicylphenetidedide* melts at 140°; *salicylanisidide* crystallises in clusters of long, slender needles melting at 159—160°, *salicyl-diphenylamide* in prisms melting at 193°, and *salicylphenylhydrazide* in leaflets melting at 131°. The salicylic esters of phenols are easily obtained when salol is heated with the respective phenols. The following are described: *Salicyl Eugenol*, small prisms, melting at 73°; *β-naphthyl salicylate*, crystalline, melting at 95°; *salicylcarvacrol*, an oil; *salicyl-m-cresol*, leaflets, melting at 170°; *salicyl-p-acetaminophenol* ("salophen"), crystalline, melting at 185°; *salicyl-p-aminophenol*, needles, melting at 168—169°; *disalicyl-p-aminophenol*, melting at 176°; *monosalicyltresorcinol*, melting at 137°; *salicylquinol*, slender leaflets, melting at 96—98°; *disalicylquinol*, thick leaflets, melting at 150—151°. Salol, when heated with salicylamide, yields *disalicylamide*, which crystallises in bright yellow, long needles melting at 200—203°.

Phenyl *p*-cresotate reacts with phenols in a similar manner: *β-naphthyl p-cresotate* crystallises in white leaflets melting at 103—104°, *resorcinyl di-p-cresotate* in slender needles melting at 106—107°, and *quinylyl di-p-cresotate* in clusters of long needles melting at 197—198°.

Phenyl cinnamate, when treated with guaiacol, yields *cinnamylguaiacol*, which melts at 121°. R. H. P.

Synthesis of *p*-Methoxyhydratropic Acid. By J. BOUGAULT (*Compt. rend.*, 1900, 131, 270—272).—*p*-Hydroxyhydratropic acid, prepared by Trinius' method (*Abstr.*, 1885, 529), melts at 130°, and was assumed by him to be identical with phloretic acid (m. p. 128°), but this is not the case, as *p*-methoxyhydratropic acid prepared from it melts at 57°, whilst the methyl derivative of phloretic acid melts at 101°. On the other hand, the acid obtained by the action of

hydriodic acid on the methoxyhydratropic acid derived from anethole (this vol., i, 495) is identical with *p*-hydroxyhydratropic acid.

C. H. B.

***o*-Aminosalicyclic Acid.** By OSKAR ZAHN (*J. pr. Chem.*, 1900, [ii], 61, 532—544).—*o*-Diazosalicyclic acid, $\text{CO}_2\text{H}\cdot\text{C}_6\text{H}_3\begin{smallmatrix} \text{O} \\ \diagup \diagdown \\ \text{N}:\text{N} \end{smallmatrix}$, obtained by diazotising *o*-aminosalicyclic acid [$\text{CO}_2\text{H}:\text{OH}:\text{NH}_2=1:2:3$] in glacial acetic acid solution, crystallises in lustrous, yellow needles, decomposes at 155° , and combines with resorcinol to form *resorcinol-o*-azosalicyclic acid, a dark-red, insoluble substance which does not melt below 300° . The *hydrazine* obtained by the reduction of *o*-diazosalicyclic acid is a very unstable substance, but condenses readily with pyruvic acid, forming the *hydrazone*, $\text{CO}_2\text{H}\cdot\text{C}_6\text{H}_3(\text{OH})\cdot\text{NH}\cdot\text{N}:\text{CMe}\cdot\text{CO}_2\text{H}$, which melts at 205° .

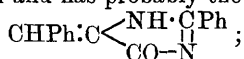
The following derivatives of *o*-aminosalicyclic acid are described: *Formyl-o*-aminosalicyclic acid, grey needles decomposing at 215° ; *hydroxycarboxyphenylaminoacetic acid*, $\text{CO}_2\text{H}\cdot\text{C}_6\text{H}_3(\text{OH})\cdot\text{NH}\cdot\text{CH}_2\cdot\text{CO}_2\text{H}$, small leaflets melting at 220° ; the *anhydride*, $\text{CO}_2\text{H}\cdot\text{C}_6\text{H}_3\begin{smallmatrix} \text{O}-\text{CO} \\ \diagup \diagdown \\ \text{NH}-\text{CH}_2 \end{smallmatrix}$, small needles melting at $174-175^\circ$, and its *ethyl ester*, a crystalline compound decomposing at 231° ; *ethenyl-o*-aminosalicyclic acid, $\text{CO}_2\text{H}\cdot\text{C}_6\text{H}_3\begin{smallmatrix} \text{O} \\ \diagup \diagdown \\ \text{N} \end{smallmatrix}\text{CMe}$, a crystalline substance melting at 245° ; *carbamidodisalicyclic acid*, $\text{CO}[\text{NH}\cdot\text{C}_6\text{H}_3(\text{OH})\cdot\text{CO}_2\text{H}]_2$, microscopic crystals; *ethyl carboxy-o*-aminosalicyclic acid, $\text{CO}_2\text{H}\cdot\text{C}_6\text{H}_3(\text{OH})\cdot\text{NH}\cdot\text{CO}_2\text{Et}$,

small plates melting at 155° , and the *anhydride*, $\text{CO}_2\text{H}\cdot\text{C}_6\text{H}_3\begin{smallmatrix} \text{O} \\ \diagup \diagdown \\ \text{NH} \end{smallmatrix}\text{CO}$, a crystalline substance melting above 300° ; *o*-*uramid*osalicyclic acid, $\text{CO}_2\text{H}\cdot\text{C}_6\text{H}_3(\text{OH})\cdot\text{NH}\cdot\text{CO}\cdot\text{NH}_2$, a crystalline substance decomposing at 215° ; *phenylsulphone-o*-aminosalicyclic acid, $\text{CO}_2\text{H}\cdot\text{C}_6\text{H}_3(\text{OH})\cdot\text{NH}\cdot\text{SO}_2\text{Ph}$, small prisms melting at 194° ; *allylthiocarbamido-o*-salicylic acid, $\text{CO}_2\text{H}\cdot\text{C}_6\text{H}_3(\text{OH})\cdot\text{NH}\cdot\text{CS}\cdot\text{NH}\cdot\text{C}_3\text{H}_5$, small prisms melting at 156° ; *phenylthiocarbamido-o*-salicylic acid, crystalline clusters decomposing at 263° ; *benzylidene-o*-aminosalicyclic acid, $\text{CO}_2\text{H}\cdot\text{C}_6\text{H}_3(\text{OH})\cdot\text{N}:\text{CHPh}$, a yellowish, crystalline substance which does not melt below 300° ; *o*-hydroxybenzylidene-*o*-aminosalicyclic acid, a yellowish substance melting at 207° .

R. H. P.

α -Amino-acids. By EMIL ERLÉNMEYER, jun. (*Ber.*, 1900, 33, 2036—2041).— α -Benzoylamino-cinnamide, $\text{C}_{16}\text{H}_{14}\text{O}_2\text{N}_2$, obtained by the action of alcoholic ammonia on α -benzoylamino-cinnamic anhydride, crystallises from dilute alcohol in long, colourless needles melting at 168° . It is very stable towards mineral acids, but quickly attacked by sodium hydroxide solution, to which it imparts a yellow or yellowish-red colour. On precipitating the alkaline solution with hydrochloric acid, a small quantity of benzoylamino-cinnamic acid is formed, the principal product being, however, an intensely yellow precipitate, which crystallises from alcohol in yellow needles decomposing at 270° .

This *substance* is neutral and has probably the constitution



it is moderately soluble in glacial acetic acid and also in hot sodium hydroxide or carbonate solution, from which it is deposited unchanged. By prolonged boiling of a solution of the amide in acetic anhydride, it becomes reddish-yellow and part of the amide is reconverted into the anhydride, whilst if the boiling is still further continued, a pasty, red resin is formed. Boiling with quinoline converts the amide into anhydride.

The action of aniline on α -benzoylamino-cinnamic anhydride gives rise to the corresponding *anilide*, $\text{C}_{22}\text{H}_{18}\text{O}_2\text{N}_2$, which crystallises in colourless needles, melts at 238° and dissolves in glacial acetic acid. It is very stable towards acids and alkalis, but on prolonged boiling with acetic anhydride undergoes decomposition, yielding two substances, one yellow and the other colourless.

On strongly heating piperidine with α -benzoylamino-cinnamic anhydride, the *piperidide* of the acid $\text{C}_{21}\text{H}_{22}\text{O}_2\text{N}_2$ is formed; this separates in massive, colourless crystals, melts at 178° , and dissolves readily in chloroform or glacial acetic acid. It strongly resists the action of acids or alkalis, and on continued heating with acetic anhydride is converted into the anhydride of the acid.

These reactions throw doubt on the view expressed by the author (*Annalen*, 1893, **275**, 6; *Abstr.*, 1899, i, 759) that internal anhydrides of acids containing the group $\cdot\text{CH:C}(\text{CO}_2\text{H})\cdot\text{NH}\cdot\text{CO}\cdot\text{R}$
 $\cdot\text{CH:C}\cdot\text{N}\cdot\text{CO}\cdot\text{R}$

have the constitution $\begin{matrix} \diagup \\ \text{CO} \end{matrix}$; thus, in the case of α -benzoylaminocinnamic acid the internal anhydride may be formed from the tautomeric modification of the formula $\text{CHPh:C}(\text{CO}_2\text{H})\cdot\text{N:CPh}\cdot\text{OH}$, and would then have the constitution $\text{CHPh:C} \begin{cases} \text{N}=\text{CPh} \\ \text{CO}\cdot\text{O} \end{cases}$.

T. H. P.

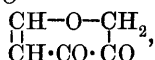
Removal of a Sulpho-group by Reduction. By F. J. MOORE (*Ber.*, 1900, **33**, 2014—2015).—When *p*-sulphocinnamic acid is reduced by means of sodium amalgam or amalgamated aluminium, the sulphydrocinnamic acid expected is not obtained, as the sulphydro-group is split off and the resulting cinnamic acid reduced to hydrocinnamic acid.

T. H. P.

Pyrone Group. VI. Constitution of Meconic, Comenic, and Pyromeconic Acids. By ALBERTO PERATONER and G. LEONARDI (*Gazzetta*, 1900, **30**, i, 539—565. Compare *Abstr.*, 1898, i, 69).—By the action of barium hydroxide on meconic, comenic, and pyromeconic acids, strongly reducing volatile compounds having a peculiar odour are obtained, but could not be isolated. With phenylhydrazine acetate, these products give an unstable, oily phenylhydrazone, but on heating with excess of the reagent, yield the same *phenylosazone*, $\text{C}_8\text{H}_6(\text{N}_2\text{HPh})_3$, which forms a straw-yellow, crystalline powder, rapidly undergoes change, and melts at 238 — 240° when plunged into a previously heated bath; it dissolves slightly in benzene, but is almost insoluble in the

other organic solvents. The osazone *dibromide*, $C_6H_6Br_2(N_2HPh)_3$, crystallises from benzene in orange-yellow, microscopic needles melting at $258-260^\circ$. On hydrolysing acetylcarbonyl acetate with barium hydroxide, an unsaturated, strongly reducing, oily product is obtained which yields the same phenylosazone as that just described (compare following abstract). Hence the first product of the action of barium hydroxide on these acids is acetylcarbinol, and in presence of excess of the base 2 mols. of this alcohol condense with the elimination of $2H_2O$ and the formation of the compound $C_6H_8O_2$. Quantitative study of the acids formed during the hydrolysis of the three acids shows that meconic acid yields 2 mols. of oxalic acid, comenic acid 1 mol. of oxalic acid and 1 mol. of formic acid, and pyromeconic acid 2 mols. of formic acid. In all three cases, small quantities of resinous substances are formed, besides which the acid products undergo more or less further oxidation, resulting in the formation of carbon dioxide and, especially with pyromeconic acid, small quantities of methyl alcohol.

The conclusion is drawn that meconic acid is 2:6-dicarboxy-3-hydroxy-1:4-pyronic acid (3-hydroxychelidonic acid), which confirms the suggestion of Brühl, Hjelt, and Aschan; comenic acid has the constitution $CO_2H \cdot C \begin{smallmatrix} \diagup O-CH \\ \diagdown CH-CO \end{smallmatrix} > C \cdot OH$ and pyromeconic acid



the last-named reacting also in the enolic form.

T. H. P.

Pyrone Group. VII. A Condensation Product of Acetylcarbinol. By ALBERTO PERATONER and G. LEONARDI (*Gazzetta*, 1900, 30, i, 565—576).—By cautious hydrolysis of acetylcarbonyl acetate, the oily *condensation product*, $C_6H_8O_2$ (see preceding abstract), is obtained as a colourless liquid with an odour recalling that of acetophenone. It is heavier than water and boils with slight decomposition at 185° under the ordinary pressure, but unchanged at 105° under 20 mm. pressure, and does not solidify at -15° . It dissolves in the organic solvents and water, is volatile in a current of steam, and reduces Fehling's solution and ammoniacal silver nitrate solution. When oxidised with permanganate or chromic acid, it yields only acetic acid. With phenylhydrazine acetate in the cold, it yields the unstable oily *phenylhydrazone* soluble in water, and, on heating, the phenylosazone, melting at $238-240^\circ$, described in the preceding paper. Its *semi-carbazone*, $(C_6H_8O)N_3H_2CO$, melts at 190° with previous softening at some degrees lower, and on attempting to crystallise it from alcohol an oxidation *product*, $(C_6H_4O_3)N_3H_3CO$, is obtained in lustrous crystals melting at 231° . The oily condensation product is dissolved by, but does not react with, acid chlorides. With bromine, an oily *dibromide* is obtained which evolves hydrogen bromide and resinifies on distillation. The constitution assigned to the condensation product is $CMe \begin{smallmatrix} \diagup CH_2-O \\ \diagdown CH-CO \end{smallmatrix} > CH_2$, that of the phenylosazone (phenyltrihydrazone) being $N_2HPh \cdot CH \cdot CMe \cdot CH \cdot C(N_2HPh) \cdot CH \cdot N_2HPh$.

T. H. P.

Ethyl Dimethylpyronedicarboxylate. By RICCARDO OLIVIERI-TORTORICI (*Gazzetta*, 1900, 30, i, 514—525).—When reduced with either zinc and hydrochloric acid or sodium amalgam and excess of acetic acid, ethyl dimethylpyronedicarboxylate does not yield ethyl dimethyltetrahydropyronedicarboxylate (Abstr., 1896, i, 472) as would be expected, but in both cases a faintly yellow, heavy oil of the composition $C_{18}H_{18}O_6$ (?), is obtained. It is very soluble in alcohol, ether, and other organic solvents, and is only slightly volatile in a current of steam. With ferric chloride solution, it gives an intense red coloration and in alcoholic solution instantly decolorises dilute potassium permanganate solution, but no additive compound with bromine could be prepared. Benzoyl chloride, hydroxylamine, phenylhydrazine, and semicarbazide are without action on the oil, which, with ammonia, yields a small quantity of a crystalline, nitrogenous compound melting at 180° . On dry distillation in a vacuum, the oil yields ethyl acetoacetate, carbon dioxide, and ethylene (?); the same products are obtained when ethyl dimethylpyronedicarboxylate itself is distilled.

By the action of semicarbazide on ethyl dimethylpyronedicarboxylate in presence of fused sodium acetate, a condensation product, $C_{14}H_{19}O_6N_3$, is obtained; it crystallises from alcohol in white needles which dissolve slightly in water, but readily in ether, and melt and evolve gas at 270° . T. H. P.

Velocity of the Reaction between Sodium Hydroxide and Benzaldehyde. By CÆSAR POMERANZ (*Monatsh.*, 1900, 21, 389—406).—The reaction between sodium hydroxide and benzaldehyde takes place in two stages (compare Kohn and Trantom, *Trans.*, 1899, 75, 1155); the first of these is the production of an additive compound, $(Ph \cdot CHO)_2NaOH$, which is formed by the undissociated sodium hydroxide, and is of the third order; the second is the decomposition of the additive compound into benzyl alcohol and the ions of sodium benzoate, and is of the first order. R. H. P.

Action of Nitric Acid on Vanillin. By WILLIAM B. BENTLEY (*Amer. Chem. J.*, 1900, 24, 171—181).—With 5 per cent. nitric acid at 50° , vanillin yields 50 per cent. of its weight of nitrovanillin along with dinitroguaiacol and an insoluble amorphous substance melting above 390° , which is probably identical with Tiemann's dehydrodivanillin (Abstr., 1886, 238). Nitrovanillin [$CHO : OMe : OH : NO_2 = 1 : 3 : 4 : 5$] is best prepared by nitrating vanillin with fuming nitric acid in cold glacial acetic acid, and crystallises well from this solvent; it melts at 176° , forms an orange-yellow, efflorescent potassium salt, $C_8H_6O_4NK \cdot H_2O$, and yields dinitroguaiacol on warming with dilute nitric acid. When oxidised with slightly alkaline potassium permanganate, it gives a nitrovanillic acid which crystallises from glacial acetic acid in light yellow, efflorescent plates containing $1\frac{1}{2}C_8H_4O_2$, melts at 216 — 216.5° , and is probably identical with Weselsky and Benedikt's acid (Abstr., 1882, 1200). W. A. D.

Nitroketones and Orthonitro-derivatives. By ANGELO ANGELI (*Atti Real. Accad. Lincei*, 1900, [v], 9, i, 41—47).—With reference to

the work of Lucas (Abstr., 1899, i, 433) and of Hantzsch (Abstr., 1899, i, 399, 401) on nitroketones, the author calls attention to the fact that, in conjunction with Rimini (Abstr., 1896, i, 295), he has obtained a compound probably belonging to that class of substances. This compound, nitropiperonylacetone, $\text{CH}_2\text{O}_2 \cdot \text{C}_6\text{H}_3 \cdot \text{CH}_2 \cdot \text{CO} \cdot \text{CH}_2 \cdot \text{NO}_2$, obtained by boiling safrole nitrosite with alcohol, reacts readily with semicarbazide yielding the corresponding *semicarbazone* which crystallises from benzene in lustrous, colourless scales melting at 151° . Instead of the name nitroic acid given by Hantzsch (this vol., i, 89) to the parent substance from which additive compounds of nitro-derivatives with sodium hydroxide or alkyl oxide may be considered to be derived, the author proposes the name orthonitric acids as being more suitable.

T. H. P.

Action of Nitrogen Tetroxide on Quinonedioximes. By RICCARDO OLIVERI-TORTORICI (*Gazzetta*, 1900, 30, i, 526—538. Compare Abstr., 1898, i, 657).—Nitrogen peroxide first oxidises the dioximes to peroxides and then diazotises one of the NO groups, yielding unstable nitrates of nitrosodiazocompounds, which readily give up nitrogen, forming the *p*-dinitro-derivatives of the corresponding hydrocarbons. That the primary action is one of oxidation is shown by the fact that dinitrosocymene and thymoquinonedioxime yield the same product on treatment with nitrogen peroxide.

With 1 mol. of nitrogen peroxide, benzoquinonedioxime and toluquinonedioxime both yield resinous products gradually decomposing with the formation of *p*-dinitrobenzene and *p*-dinitrotoluene respectively. With thymoquinonedioxime, which is best prepared by the action of hydroxylamine hydrochloride on nitrosocarvacrol, *nitrosodiazocymene nitrate*, $\text{C}_{10}\text{H}_{12}\text{O}_4\text{N}_4 [\text{N}_2 \cdot \text{NO}_3 : \text{Me} : \text{NO} : \text{Pr}^s = 1 : 3 : 4 : 6 \text{ or } 1 : 6 : 4 : 3]$, is obtained and forms light, canary-yellow flocks which, under the action of heat or percussion, decompose violently; on heating in a capillary tube, decomposition occurs at $56\text{--}60^\circ$. It gives Liebermann's nitroso-reaction, and when treated in alcoholic solution with β -naphthol or resorcinol produces the intense red coloration characteristic of diazo-compounds. Its ethereal solution slowly decomposes, yielding *p*-dinitrocymene.

Impure naphthaquinonedioxime (containing nitrosonaphthol) and nitrogen peroxide yield *nitrosodiazonaphthalene nitrate* in the form of unstable yellow flocks which explode when heated or struck, and could not be analysed. In ethereal solution, it decomposes, giving the corresponding dinitronaphthol.

The action of nitrogen trioxide on thymoquinonedioxime and the corresponding dinitroso-compound yields the same product as is obtained when the peroxide is employed.

T. H. P.

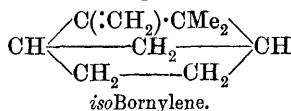
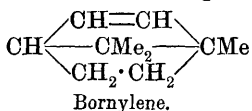
Hydroxymethylanthraquinones. By PIO MARFORI (*Chem. Centr.*, 1900, i, 1292; from *Ann. Farm. Chim.*, 1900, 85—95).—Chrysophanic acid occurs apparently in two isomeric forms which melt at 162° and 178° respectively. Isomeric acids melting at 162° and 191° respectively were also obtained by the oxidation of chrysarobin. The chrysophanic acid, prepared by passing a stream of air through a solution of chrysarobin in alcoholic potash for 6 days, crys-

tallises in golden-yellow, rhombohedral plates, melts at 162—163°, is soluble in alcohol, ether, benzene, alkalis, or sulphuric acid, but almost insoluble in cold ammonia or alkali carbonates, and insoluble in water; it is not a purgative. From the crude product of the oxidation of chrysarobin, a yellow and a red substance were also obtained by sublimation; the former melts at 160—175°, and the latter at 180—184°.

In an appendix to the original paper an oxidation product of chrysarobin melting at 162—187° is described which appears to contain several isomerides; it has a strong purgative action. Chrysarobin does not act as a purgative.

E. W. W.

Bornylene, a New Terpene. By GEORG WAGNER and WACLAU BRYKNER (*Ber.*, 1900, 33, 2121—2125).—By heating pinene hydriodide with potassium phenolate to 160—170°, instead of with alcoholic potash, camphene is obtained without admixture with a second hydrocarbon. This other hydrocarbon (*Abstr.*, 1900, i, 47) can be obtained in better yield than formerly by employing 40 per cent. alcoholic potash and heating in an autoclave at 170° for 4 hours. The product was fractionated, and the fraction boiling at 152—160° heated with acetic acid at 55—60° in a sealed tube, when the camphene was converted into *isobornyl* acetate, whilst the new terpene remained unattacked, and was separated by fractionation. This terpene, $C_{10}H_{16}$, melts at 97·5—98°, boils at 149—150° under 750 mm. pressure, and sublimes very rapidly even at the ordinary temperature; it is oxidised by dilute aqueous potassium permanganate at the ordinary temperature to camphoric acid. It is the true camphene, corresponding with camphor and borneol, and should be named *bornylene*; for the other camphene, which is oxidised by permanganate to camphenecamphoric and camphenylic acids, and camphenylone, the name *isobornylene* is proposed. The following are the constitutions assigned:

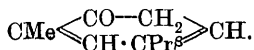


Probably bornylene has been obtained already by Spitzer (*Annalen*, 1879, 197, 129).

C. F. B.

Isocamphor. By ENRICO RIMINI (*Gazzetta*, 1900, 30, i, 596—600. Compare Angeli and Rimini, *Abstr.*, 1897, i, 88).—To determine whether *isocamphor* contains the group $\cdot\text{CO}\cdot\text{CH}_2\cdot$ or $\cdot\text{CO}\cdot\text{CHPr}^\beta\cdot$, attempts were made to obtain condensation products of it with aldehydes, but without success. With dihydroisocamphor, however, this is possible, and on mixing it with 1 mol. of benzaldehyde and gradually adding an alcoholic solution of sodium ethoxide (1 mol.), *benzylidenedihydroisocamphor*, $C_{10}H_{16}O\cdot\text{CHPh}$, is obtained; it crystallises from alcohol in small, white needles melting at 217°. Hence *isocamphor* contains the group $\cdot\text{CO}\cdot\text{CH}_2\cdot$, and its constitution is

$\text{CMe} \begin{array}{l} \nearrow \text{CO} \text{---} \text{CH}_2 \\ \searrow \text{CH} \cdot \text{CHPr}^\beta \end{array} \text{CH}_2$, that of isocamphenone being



T. H. P.

Researches in the Camphor Group. By ENRICO RIMINI (*Gazzetta*, 1900, 30, i, 600—604).—Tanacetoneoxime, on treatment with amyl nitrite, yields crystals consisting probably of tanacetylimine nitrate. By the action of nitrous acid, it yields a *pernitroso*-derivative (compare Abstr., 1895, i, 426; 1897, i, 87, 88, 90), which decomposes on heating, evolving red vapours, and when distilled in a current of steam in presence of potassium hydroxide yields tanacetone and nitrous oxide; with hydroxylamine, tanacetoneoxime is regenerated, whilst by the action of concentrated sulphuric acid, nitrous oxide is formed, together with an oil which has a peculiar odour and is volatile in a current of steam. When treated in alcoholic solution with the calculated quantities of semicarbazide hydrochloride and sodium acetate, the pernitroso-compound gives rise to tanacetone semicarbazone, which separates in needles melting at 178° ; the same melting point is given by the carbazone when prepared directly from tanacetone, whilst this temperature is given in the literature as 271° . In a similar manner, pernitrosomenthone yields menthone semicarbazone melting at 192 — 193° , whilst that prepared from menthone melts at 185° ; also pernitrosocamphor gives camphor semicarbazone, which is only with difficulty obtained directly from camphor. With pernitrosufenchone, however, the action in the cold of semicarbazide acetate is similar to that of alcoholic ammonia, the product in both cases being *isopernitrosufenchone*; when heated gently on the water-bath, however, pernitrosufenchone and semicarbazide acetate yield *fenchone semicarbazone*, $C_{10}H_{16}\cdot N\cdot NH\cdot CO\cdot NH_2$, which separates from alcohol in white crystals melting at 186 — 187° , and cannot be obtained directly.

T. H. P.

Neroli (Orange Blossom) Oil. By ERNST ERDMANN and HUGO ERDMANN (*Ber.*, 1900, 33, 2061—2062).—A claim for priority (see H. Walbaum, Abstr., 1899, i, 620, 621).

R. H. P.

Origin of and Relations between the Glucosides of *Strophanthus*. By FRANZ FEIST (*Ber.*, 1900, 33, 2063—2069. Compare Abstr., 1898, i, 328, 329).—The very variable physiological action of the pharmaceutical preparations of *Strophanthus* has been due, (1) to the indiscriminate use of different species of *Strophanthus* seeds (principally of *Strophanthus kombé* and *S. hispidus*), some of which contain no glucoside, and (2) to the existence of two glucosides, strophanthin and ψ -strophanthin, of which the latter is three or four times as strong a poison as the former.

Strophanthin has the formula $C_{40}H_{66}O_{19}$, and, when hydrolysed, yields strophanthidin, $C_{27}H_{38}O_7\cdot 2H_2O$, and a sugar, $C_{12}H_{21}O_9\cdot OMe$ (see this vol., i, 540); ψ -strophanthin has the formula $C_{40}H_{66}O_{16}$, and, when hydrolysed, yields ψ -strophanthidin, $C_{27}H_{37}O_5\cdot OMe$, and a sugar, which has not been isolated.

R. H. P.

Strophanthin and Strophanthidin. By FRANZ FEIST (*Ber.*, 1900, 33, 2069—2090. Compare Abstr., 1898, i, 329).—Strophanthin, $C_{40}H_{66}O_{19}\cdot 3H_2O$, is very hygroscopic, but when dried over sulphuric acid, becomes anhydrous and melts then at 170° ; its specific rotation

in water is $[\alpha]_D + 10 \cdot 12^\circ$. When hydrolysed with very dilute hydrochloric acid, it yields strophanthidin, $C_{27}H_{38}O_7$, which crystallises with $\frac{1}{2}H_2O$ in lustrous, monoclinic prisms $\{a:b:c = 1 \cdot 1275 : 1 : 1 \cdot 1179 ; \beta = 70^\circ 52'\}$, which melts at $169-170^\circ$, froths at 176° , solidifies on cooling, and then melts at 232° (the melting point of the pure anhydrous substance being 235°). Its specific rotation in methyl alcohol is $[\alpha]_D + 45 \cdot 45^\circ$.

Strophanthidin, when treated with alkalis and then acidified, yields the isomeric strophanthidic lactone, $C_{27}H_{38}O_7 \cdot \frac{1}{2}H_2O$, which melts at 243° , has been previously described (*loc. cit.*) as having the formula $(C_7H_{10}O_2)_x$, and, when further treated with alkalis, yields anhydrostrophanthidic lactone, $C_{27}H_{34}O_5$ (*loc. cit.*), which melts at 345° (corr.), and a brown acid compound, $C_{26}H_{36}O_6$, which melts and decomposes at 180° . Strophanthidin or strophanthidic lactone, when oxidised with potassium permanganate in alkaline solution, yields *strophanthic acid*, $C_{27}H_{38}O_9$, which crystallises in clusters melting at $260 \cdot 8^\circ$, forms a monohydrate, which crystallises in small needles melting at $190 \cdot 7^\circ$ and an insoluble *silver* salt, $C_{27}H_{40}O_{11}Ag_2 \cdot H_2O$, which is derived from a dihydrate of the acid.

R. H. P.

Chemistry of the Cell Membrane of Mosses and Liverworts. By FRIEDRICH CZAPEK (*Chem. Centr.*, 1900, i, 1031; from *Flora*, 86, 361. Compare Abstr., 1899, i, 560).—The cell membranes of mosses and liverworts do not as a rule give the reactions of cellulose directly, but only after more or less prolonged boiling with sodium hydroxide solution. The cell walls of the mosses form an intense yellow coloration with sodium hydroxide solution, and they also, for the most part, either give Millon's reaction or produce a blackish-green coloration with salts of iron. *Sphagnum* gives Millon's reaction most distinctly, and from this moss *sphagnol* was isolated by prolonged boiling with a 1 per cent. solution of sodium hydroxide under pressure. This compound is found especially in mosses which grow in damp places, appears to be phenolic in character, gives an intense cherry-red coloration with Millon's reagent, and has rather strong antiseptic properties. The dark green iron reaction of the mosses is probably due to the presence of *dicranumtannic acid*, which may be extracted by prolonged boiling with water under pressure.

E. W. W.

Phytochemical Studies. I. Distribution of Alkaloids in the Compositæ. By M. GRESHOFF (*Chem. Centr.*, 1900, i, 1297; from *Ned. Tijd. Pharm.*, 12, 137—146).—A list of *Compositæ* which contain alkaloids is quoted. Of 150 different kinds examined, 50 were found to contain alkaloids. The fruit of *Echinops Ritro* contains 0.5 per cent. of *echinopsine*, $C_{11}H_9ON$, which forms rhombic crystals, melts at 152° , is easily soluble in chloroform, hot benzene, or hot water, and slightly so in ether. With ferric chloride, it gives a blood-red coloration. The following salts were prepared: *hydrochloride*, with $2H_2O$; *sulphate*, with $2H_2O$ and $8H_2O$; *nitrate*, with $3H_2O$; *oxalate*, with $4H_2O$; *mercuriodide*, $(C_{11}H_9ON, HI)_2, HgI_2$. The poisonous action of this alkaloid is similar to that of a mixture of strychnine and brucine.

E. W. W.

Cotarnine Cyanide as a Pseudo-salt. By ARTHUR HANTZSCH and M. KALB (*Ber.*, 1900, **33**, 2201—2208. Compare this vol., i, 115, 248).—Cotarnine cyanide, like *syn*-diazocyanides, in absolute alcoholic solution is scarcely and, even in 50 per cent. alcohol, only very slightly ionised to cotarninium cyanide, the value for μ being only about 1/30th that of μ for potassium cyanide under similar conditions. In aqueous solution, the conductivity is also small, but rapidly increases with rise of temperature from 0° to 40°; the temperature coefficient also rapidly increases, and is 0.1465 between 0° and 40°, whereas for a true salt it is constant, and usually about 0.02°.

At higher temperatures, decomposition into the free base and hydrogen cyanide occurs.

When a few bubbles of carbon dioxide are passed into an aqueous solution of the cyanide, the colour changes to yellow and the conductivity increases considerably, probably owing to the formation of cotarninium carbonate.

Mixtures of diazonium chloride with potassium cyanide and of cotarninium chloride with potassium cyanide give constant results for their conductivities in either alcoholic or aqueous solution at 25°, whereas a mixture of cotarninium chloride with potassium cyanide in aqueous solution at 0° gives, immediately after mixing, much higher conductivities, which slowly sink to the constant value. The authors explain this phenomenon by assuming that the true cotarninium cyanide is first formed, and that this is then slowly isomerised to the non-dissociated cotarnine cyanide.

The following are given as characteristics of *pseudo*-salts: As true organic compounds, they are soluble in different organic solvents, not merely in alcohol, ether, or pyridine, but also in benzene, chloroform, or light petroleum. In solvents of the water type, and more especially in water itself, they become more or less isomerised, and at the same time ionised into the ions of the true salt, which is not stable in the solid state.

J. J. S.

Reduction of Succinimides to Pyrrolidones. By JULIUS TAFEL and MAX STERN (*Ber.*, 1900, **33**, 2224—2236).—A 60 per cent. yield of pyrrolidone may be obtained by the electrolytic reduction of a solution of succinimide in 50 per cent. sulphuric acid.

Pyrrolidone (compare Gabriel, *Abstr.*, 1890, 360) melts at 24.65°, boils at 250.5° under 742 mm. pressure, has a sp. gr. 1.120 at 20°/4°, 1.116 at 25°/4°, 1.110 at 30°/4°, 1.097 at 40°/4°. The hydrate $C_4H_7ON \cdot H_2O$ melts at 29.3—30.6, and solidifies at 29.7—29.9°. On the addition of nitric acid to a hot solution of pyrrolidone and phosphotungstic acid, a crystalline product is obtained. *Mercury pyrrolidone*, $(C_4H_6ON)_2Hg \cdot H_2O$, crystallises in colourless needles, loses its water at 100°, turns brown at 180°, and melts and decomposes at 218°. *Bromopyrrolidone*, C_4H_6ONBr , crystallises from benzene in rectangular plates, melts at 95°, is decomposed when boiled with water or treated with sodium hydroxide. *Acetylpyrrolidone*, C_4H_6ONAc , is a colourless oil distilling at 229—233°.

When pyrrolidone is boiled with alkalis, concentrated hydrochloric acid, or barium hydroxide, it is converted into γ -aminobutyric acid,

melting and decomposing at 202° (Gabriel gives 184°). The acid yields a hydrochloride which is not hygroscopic (compare Schotten, Abstr., 1883, 813), an *aurichloride*, a brick-red precipitate with potassium bismuthiodide, and a *silver salt*, $C_4H_8O_2NAg$, soluble in warm water. The *hydrochloride* of the ethyl ester melts at $65-72^{\circ}$.

iso*Propylsuccinimide* is a colourless, crystalline substance melting at 60° and distilling at 225° under 743 mm. pressure. It dissolves easily in most organic solvents, is readily volatile with steam, and when electrolytically reduced yields *isopropylpyrrolidone*; this is a colourless oil which distils at $220.5-222^{\circ}$ under 736 mm. pressure, and differs from pyrrolidone itself in its greater volatility with steam, and in not undergoing hydrolysis when boiled with barium hydroxide.

Ethylpyrrolidone, obtained by the electrolytic reduction of acetylpyrrolidone at temperatures below 45° , is a colourless oil distilling at 218° under 751 mm. pressure. *p-Tolylpyrrolidone*, obtained by the reduction of the corresponding succinimide in 95 per cent. sulphuric acid, crystallises from light petroleum in colourless needles melting at 88.5° , and is completely soluble in 50 per cent. sulphuric acid.

J. J. S.

A New Trimethylpyridine. By ICILIO GUARESCHI (*Chem. Centr.*, 1900, i, 1161; from *Atti Real. Accad. Torino*, 35).—By heating 3-cyano-4:5:6-trimethylpyridone with powdered zinc in a stream of hydrogen at a dark red heat, hydrogen cyanide is liberated, and a liquid formed which yields two fractions boiling at $180-195^{\circ}$ and $260-270^{\circ}$ respectively. The latter consists of 4:5:6-trimethylpyridone, which is an intermediate product of the reduction of the pyridone. The fraction of lower boiling point contains 4:5:6-trimethylpyridine; it has a pungent, pyridine-like odour, boils at $185-188^{\circ}$, has a sp. gr. 0.9127 at 15° , becomes yellow on exposure to air, dissolves in water forming an alkaline solution, and is easily soluble in alcohol or ether. A saturated aqueous solution becomes turbid on only very slightly warming. With copper sulphate, the aqueous solution gives a blue and with ferric chloride a brick-red precipitate. The *hydrochloride* crystallises in white, deliquescent needles, the *platini-chloride* in yellow prisms melting at $211-212^{\circ}$, the *aurichloride* in yellow needles melting at about 100° , and the *picrate* in yellow forms. Trimethylpyridine is oxidised by potassium permanganate, forming Weidel's carbocinchomeric acid (4:5:6-pyridinetricarboxylic acid).

E. W. W.

Action of Iodine on a Pyridine Solution of Malonic Acid. By GIOVANNI ORTOLEVA (*Gazzetta*, 1900, 30, i, 509-514).—The action of iodine on cinnamic acid in pyridine solution gives rise to pyridine β -iodocinnamate (Abstr., 1899, i, 894), but by gradually adding iodine (1 mol.) to a solution of malonic acid (1 mol.) in pyridine, a *basic hydriodide of pyridinebetaine*, $C_5NH_5I \cdot CH_2 \cdot CO_2H, C_5NH_5 \langle \overset{CH_2}{O} \rangle CO_2$, is obtained. This compound crystallises from alcohol in massive, long white needles, which blacken at $175-180^{\circ}$ and melt and decompose at $250-252^{\circ}$; it is moderately soluble in alcohol and very soluble in water, giving an acid solution. On treatment with sodium carbonate

or silver hydroxide, pyridinebetaine is obtained, whilst sodium hydroxide solution dissolves it, giving a colourless liquid which on heating becomes brown, pyridine at the same time being set free. On reduction with sodium amalgam, or with zinc and hydrochloric acid, and neutralising with potassium hydroxide, a beautiful azure-blue coloration is produced, which disappears on shaking in the air, but reappears on standing or warming.

The formation of the pyridinebetaine compound is probably due to the decomposition of the iodomalonic acid first formed into carbon dioxide and iodoacetic acid (compare Angeli, *Abstr.*, 1893, i, 307); in presence of excess of pyridine, the iodoacetic acid acts similarly to chloroacetic acid, which yields the corresponding basic hydrochloride of pyridinebetaine (*Abstr.*, 1891, 941). T. H. P.

Preparation of 4-Pyridinecarboxylic Acid and some of its Derivatives. By LUDWIG TERNÁJGÓ (*Monatsh.*, 1900, 21, 446—460).—Methyl isonicotinate is obtained to the extent of about 58 per cent. of the theoretical by heating methyl silver cinchomerate; it crystallises in clusters of needles, and melts at 8·5°. The *hydrochloride* crystallises in large, white plates or needles decomposing at 257°, the *platinichloride* in lustrous, orange-red needles melting at 174—175°, the *methiodide* in long, scarlet-red needles and prisms decomposing at 183—184°. *isoNicotinic methylbetaine*, $C_7H_7O_2N \cdot H_2O$, obtained from the methiodide by the action of moist silver oxide, crystallises in long, lustrous needles, and its *platinichloride*, with H_2O , in long, lustrous, yellow, triclinic needles. *isoNicotinamide* crystallises in leaflets, and melts at 155·5—156°. R. H. P.

Tripyridinechromium Trichloride and Triethylenediamine Chromium Salts. By P. PFEIFFER (*Zeit. anorg. Chem.*, 1900, 24, 279—304).—*Tripyridinechromium trichloride*, $Cr(C_5NH_5)_3Cl_3$, obtained by boiling anhydrous violet chromic chloride with excess of pyridine for 1 hour in a reflux apparatus, crystallises in green plates, is easily soluble in pyridine, sparingly so in methyl or ethyl alcohol, and is not attacked by cold water or ammonia. With water, the solution in pyridine gives a green precipitate, with ammonia a bright green, crystalline precipitate and reddish-violet solution, which, on addition of alcohol, yields a bluish-violet precipitate, and with silver nitrate, on warming, a precipitate of silver chloride.

Pyridinium pentachlorochromate, $CrCl_5(C_5NH_6)_2 \cdot 3H_2O$, is obtained by heating the preceding compound with concentrated hydrochloric acid, or by evaporating a solution of violet chromium chloride mixed with some chromous chloride in concentrated hydrochloric acid with pyridine hydrochloride. It crystallises in brownish-yellow, prismatic needles, is extremely deliquescent, dissolves in methyl or ethyl alcohol, and, when warmed with pyridine, is converted into tripyridinechromium trichloride; with silver nitrate, only part of the chlorine is precipitated. The corresponding *pentabromo-derivative*, $CrBr_5(C_5NH_6)_2 \cdot 3H_2O$, is described.

Triethylenediaminechromium chloride, $Cr(C_2H_8N_2)_3Cl_3 \cdot 3\frac{1}{2}H_2O$, is obtained by gradually adding the theoretical quantity of tripyridinechromium trichloride to ethylenediamine monohydrate. It crystallises

in orange-yellow prisms, is easily soluble in water, yielding a neutral solution, and decomposes when warmed with water or when exposed to sunlight; when treated with silver oxide, it yields a strongly alkaline solution which quickly decomposes, and gives characteristic precipitates with many metallic salts. *Triethylenediaminechromium bromide*, with $3\text{H}_2\text{O}$ or $5\text{H}_2\text{O}$; the *iodide*; the *thiocyanate*, with $1\text{H}_2\text{O}$; the *nitrate*; the *dichromate*, with $2\text{H}_2\text{O}$; the *sulphate*, and the *cobaltchloride* are described. *Triethylenediaminechromium hexacyanochromate*, $\text{Cr}(\text{C}_2\text{H}_8\text{N}_2)_3\text{Cr}(\text{CN})_6 \cdot 2\text{H}_2\text{O}$, is obtained in feathery, yellow crystals by adding potassium chromic cyanide to a concentrated solution of the chloride, and similar compounds are formed with potassium cobaltcyanide and potassium ferricyanide.

Tripropylenediaminechromium iodide, $\text{Cr}(\text{C}_3\text{H}_{10}\text{N}_2)_3\text{I}_3 \cdot \text{H}_2\text{O}$, obtained by adding potassium iodide to the product of the action of propylenediamine on tripyridinechromium trichloride, crystallises in small, yellow needles, and reacts with silver oxide in the same manner as the corresponding ethylenediamine salt. E. C. R.

Formation of Indigotin from Diphenyldiketopiperazine. By M. KUHARA and M. CHIKASHIGE (*Amer. Chem. J.*, 1900, 24, 167—170).—When diphenyldiketopiperazine is fused with potassium hydroxide, and the product dissolved in water, indigotin is obtained probably as the result of the intermediate formation of anilinoacetic acid, and pseudoindoxyl. In Flimm's synthesis of indigotin from ω -bromoacetanilide by fusion with potash (*Abstr.*, 1890, 383), diphenyldiketopiperazine is probably first formed, just as it is produced on boiling ω -chloroacetanilide with alcoholic potassium hydroxide.

W. A. D.

Oxidation [of Indigotin]. By GEORG VON GEORGIEVICS and L. SPRINGER (*Monatsh.*, 1900, 21, 413—421).—The oxidation of indigotin by chromic acid is much accelerated by the presence of oxalic acid, and in a less degree by citric, tartaric, salicylic, benzoic, succinic, malonic, acetic, or formic acid, glycerol, or alcohol; the acceleration produced is proportional to the quantity of these substances present, or, in other words, their action is catalytic. R. H. P.

[Crystalline Indigo-White.] By A. BINZ and F. RUNG (*Zeit. angew. Chem.*, 1900, 412—418).—When 10 grams of indigotin, 7 grams of zinc, 60 c.c. of alcohol, 15 c.c. of water, and 1.5 grams of calcium chloride are heated for an hour in an atmosphere of carbon dioxide and the mixture cooled, indigo-white separates in minute crystals. Two other methods of preparing indigo-white in a crystalline state are described. R. L. J.

Action of Alkyl Iodides on Indoles. By GIUSEPPE PLANCHER (*Atti Real. Accad. Lincei*, 1900, [v], 9, i, 115—122).—To obtain 1:3-dimethyl-3-ethyl-2-methylenindoline (*Abstr.*, 1899, i, 452) in a pure state, methylethylacetone phenylhydrazone was condensed by heating with alcoholic zinc chloride, by which means a zincchloride, $(\text{C}_{12}\text{H}_{15}\text{N})_2\text{ZnCl}_2$, was obtained; it crystallises from alcohol in needles melting at $200\text{--}202^\circ$, and, when treated with alkali, yields 2:3-dimethyl-3-ethylindolenine, which boils at $242\text{--}244^\circ$, and gives a picrate

melting at 152—153° and an oxime melting at 158—159°. On digesting 2:3-dimethyl-3-ethylindolenine with methyl iodide, it is transformed into 1:3-dimethyl-3-ethyl-2-methylenindoline hydriodide, which crystallises from alcohol in needles or spangles melting and decomposing at 244°; this melting point was not obtained for the compound as prepared by any one of the three ways from indole derivatives (*loc. cit.*). The picrate melts at 123—124°, which is 10° higher than previously found. On attempting to further purify the base by hydrolysing the acetyl or benzoyl compound, impure basic products were obtained, and, in the case of the latter compound, benzoic acid and acetophenone were also formed; this confirms the constitution ascribed to the benzoyl derivatives of the methylenindolines, the stability towards permanganate being explained by their capability of existing in the tautomeric form

$$\begin{array}{c} \text{CR}^1\text{R}^{11} \cdot \text{C} - \text{CH} \\ | \qquad \qquad \qquad \diagup \\ \text{C}_6\text{H}_4 - \text{NMe} \cdot \text{O} \qquad \text{CPh.} \end{array}$$

1:3-Dimethyl-3-ethyl-2-methylenindoline is also formed by the condensation of methylethyl-acetone phenylmethyldiazone.

[With ALDO BONAVIA.]—When ethyl isopropyl ketone phenylhydrazone is condensed by means of alcoholic zinc chloride, 3:3-dimethyl-2-ethylindolenine is formed, together with 3-methyl-2-isopropylindole, the latter boiling at 175—177° under 30 mm. and at 288—290° under 755 mm. pressure, and giving a dark, brick-coloured picrate melting at 165—166°. 3:3-Dimethyl-2-ethylindolenine crystallises from light petroleum in small, colourless prisms or scales which melt at 52—53°, boil at 129—130° under 25 mm. pressure, and are stable in air; the picrate melts at 137—138°, and the hydriodide at 186°; with nitrous acid, the base yields a ketoxime, $\text{C}_6\text{H}_4 \begin{array}{c} \text{CMe}_2 \\ \diagdown \quad \diagup \\ \text{N} \end{array} \gg \text{C} \cdot \text{CMe} \cdot \text{N} \cdot \text{OH}$, this being

the first instance among aromatic compounds of a change of this kind. With methyl iodide, the base yields 1:3:3-trimethyl-2-ethylidenindoline hydriodide, which melts at 185—186°, and is identical with the impure product obtained by Piccinini (*Abstr.*, 1898, i, 691) by methylating 1:3:3-trimethyl-2-methylenindoline.

As just stated, 1:3:3-trimethyl-2-ethylidenindoline hydriodide melts at 186°; if, however, it is heated slowly in a test-tube, it melts at about 220°, undergoing transformation into 1:3-dimethyl-3-ethyl-2-methylenindoline, $\text{C}_6\text{H}_4 \begin{array}{c} \text{CMe}_2 \\ \diagdown \quad \diagup \\ \text{NMe} \end{array} \gg \text{CEtI} \rightarrow \text{C}_6\text{H}_4 \begin{array}{c} \text{CMeEt} \\ \diagdown \quad \diagup \\ \text{NMe} \end{array} \gg \text{CMeI} \rightarrow \text{C}_6\text{H}_4 \begin{array}{c} \text{CMeEt} \\ \diagdown \quad \diagup \\ \text{NMeI} \end{array} \gg \text{CMe}$. This change explains the formation of 1:3-dimethyl-3-ethyl-2-methylenindoline from 2-ethyl-3-methylindole.

3-Methyl-2-isopropylindole, when treated with methyl iodide, does not yield 1:3:3-trimethyl-2-isopropylidenindoline hydriodide, but an isomeric compound (*Abstr.*, 1899, i, 454) melting at 232°, in which the isopropyl group has probably been transferred to the 3-position. There seems to be a tendency for the heavier group to pass into the 3-position, that is, to approach the benzene nucleus.

When alkyl iodides act on 2:3-disubstituted indoles at low temperatures, the hydriodide of the corresponding indolenine is formed directly and in almost quantitative yield, the alkyl iodide being simply

added on at the double linking of the indole. Thus, on heating 2:3-dimethylindole with ethyl iodide for 6 hours at 60—85°, 2:3-dimethyl-3-ethylindolenine is obtained. This affords a much simpler method of obtaining substituted indolenines than by use of ketones.

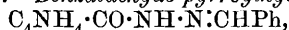
T. H. P.

Transformations of Tetrahydrocarbazole. By GIUSEPPE PLANCHER (*Atti Real. Accad. Lincei*, 1900, [v], 9, i, 218—223).—[With G. TESTONI.]—The base, $C_{14}H_{17}N$, obtained by Zanetti and Levi (Abstr., 1895, i, 54) by the action of methyl iodide on tetrahydrocarbazole, and regarded by them as a hydroacridine derivative, must, in the light of the author's work on the methylation of indole compounds, be assumed to have the constitution $\begin{array}{c} C_6H_4 \cdot CMe-CH_2 \\ | \\ NMe-C:CH \cdot CH_2 \end{array} > CH_2$.

It is obtained probably in the form of a hydrate with $1H_2O$, melts at about 57—58°, and boils at 180—181° under 31 mm. pressure. The *picrate*, $C_{14}H_{17}N, C_6H_3O_7N_3$, melts at 157—158°, and the *hydriodide* at 211°, decomposing at about 225°. On heating the base with hydriodic acid and phosphorus, it loses the N-methyl group and yields a secondary base, $C_{13}H_{15}N$, which has an odour similar to that of thymol, gives Liebermann's nitrosoamine reaction, and readily combines with phenylcarbimide. Its *hydriodide* melts at 196—197°, and the *picrate* separates from benzene in pale yellow crystals melting at about 161°. On oxidising this base with alkaline permanganate at low temperatures, it yields a *methylcarbazolenine*, $\begin{array}{c} C_6H_4 \cdot CMe-CH_2 \\ | \\ N=C-CH_2 \cdot CH_2 \end{array} > CH_2$, which gives a

picrate slightly soluble in alcohol and melting at 170°. This base is also obtained, together with a non-basic indole derivative, probably methyltetrahydrocarbazole, by condensing α -methylketo-hexamethylene phenylhydrazone in presence of alcoholic zinc chloride. T. H. P.

2-Pyrrylurethane. By ANTONIO PICCININI and L. SALMONI (*Atti Real. Accad. Lincei*, 1900, [v], 9, i, 359—361).—The *hydrazide of 2-carbopyrrolic acid*, $C_4NH_4 \cdot CO \cdot N_2H_3$, formed by heating together the methyl ester of the acid and 50 per cent. hydrazine hydrate solution in mol. proportion, melts at 231—232°, previously becoming yellow at about 210°. It has energetic reducing properties and readily condenses with aldehydes. *Benzaldehyde pyrrolylhydrazone*,



crystallises in colourless plates melting at 164—165°. With nitrous acid, pyrrolylhydrazone is completely converted into 2-pyrroylazide, $C_4NH_4 \cdot CO \cdot N_3$, which is soluble in alcohol or ether and melts at 105°, evolving gas; when heated on platinum, it deflagrates slightly, and, in presence of acid, nascent hydrogen converts it into 2-carbopyrrolamide.

2-Pyrrylurethane, $C_4NH_4 \cdot NH \cdot CO_2Et$, obtained when 2-pyrroylazide is boiled with absolute alcohol, crystallises in long, colourless laminae or flat needles melting at 55—56°. It is a basic substance, dissolves in dilute mineral acids with more or less formation of resin, and turns

red in the air. With nitrous acid, a yellow *nitroso*-derivative, $C_4NH_4 \cdot N(NO) \cdot CO_2Et$, is formed, which does not melt, but decomposes at about 200° . In acetic anhydride, 2-pyrrylurethane dissolves in the cold without change, but on heating the solution to about 50 — 60° , a crystalline *acetyl* derivative is formed together with a red compound.

T. H. P.

Ureaimino-, Thioureaimino-, and Acylthioureaimino-esters, and Ureaamidines. By HENRY L. WHEELER and W. MURRAY SANDERS (*J. Amer. Chem. Soc.*, 1900, 22, 365—378).—When phenylcarbimide, $CO \cdot NPh$, and benziminoisobutyl ester, $OBu \cdot CPh : NH$, are allowed to react at the ordinary temperature, *phenylureaiminoisobutyl benzoate*, $OBu \cdot CPh : N \cdot CO \cdot NHPh$, is formed. This melts at 99 — 100° , reacts with aniline in warm benzene solution to form *phenylbenzenylthioureaphenylamidine*, $NHPh \cdot CPh : N \cdot CO \cdot NHPh$ (which melts at 179 — 180° and is neutral in character), and is decomposed by hydrogen chloride, even in benzene solution, into isobutyl chloride and benzoylphenylcarbamide, $CPhO \cdot NH \cdot CO \cdot NHPh$. Corresponding derivatives could not be prepared from the methyl and ethyl esters and from phenylacetiminomethyl ester when the phenylcarbimide contained phosphorus oxychloride; benzoylphenylcarbamide and *phenylacetylphenylcarbamide*, $CH_2Ph \cdot CO \cdot NH \cdot CO \cdot NHPh$, were obtained at once; the latter melts at 166° .

Imino-esters react with phenylthiocarbimide in a similar way, but less readily, and form products which give analogous reactions. These products are less readily decomposed by hydrochloric acid, however; with ammonia, they yield phenylthiocarbimide, and form additive compounds with methyl iodide. The names, formulæ, and melting points of the substances prepared are: *Phenylthioureaiminomethyl benzoate*, $OMe \cdot CPh : N \cdot CS \cdot NHPh$, 132° , and the analogous *ethyl*, 119° , and *isobutyl*, 125° , compounds; *phenylbenzenylthioureap-antisylamidine*, $OMe \cdot C_6H_4 \cdot NH \cdot CPh : N \cdot CS \cdot NHPh$, 180° , and the analogous *phenyl*, 151 — 152° , and *β -naphthyl*, 182 — 183° , compounds.

Imino-esters also combine with acetyl and benzoylthiocarbimides, $CS \cdot NBz$, &c., in the same way, but even more readily; the compounds are far less stable, however. These products, as well as the amidines derived from them, form additive compounds with alkyl haloids (1 mol.); hydrochloric acid does not simply hydrolyse the alkoxyl, but eliminates the alkyl benzoate, leaving benzoylthiurea, &c. Compounds prepared: *Acetylthioureaiminoisobutyl benzoate*, 125 — 126° ; *Benzoylthioureaiminoisobutyl benzoate*, $OBu \cdot CPh : N \cdot CS \cdot NHBz$, 120° , and the analogous *ethyl* compound, 131 — 132° ; the *methiodide*, 204 — 205° , of the former, and *benzoylbenzenylthioureaphenylamidine*, $NHPh \cdot CPh : N \cdot CS \cdot NHBz$, 145 — 146° , and the analogous *o-tolylamidine*, 116 — 117° . *Benzoylthioureaiminomethylphenyl acetate*,

$OMe \cdot C(CH_2Ph) : N \cdot CS \cdot NHBz$,

116 — 117° , and the corresponding *ethyl* derivative, 140 — 141° .

The salts of the imino-esters do not react with potassium cyanate or thiocyanate to form a carbamide or a thiocarbamide, and this seems a strong argument in support of Stieglitz's theory that the

salts in question, the hydrochloride, for instance, are not ammonium derivatives, $\text{OR}\cdot\text{CR}'\cdot\text{NH}_2\text{Cl}$, but are constituted on the type $\text{OR}\cdot\text{CR}'\text{Cl}\cdot\text{NH}_2$. A constitution of this type, $\text{OBu}\cdot\text{CPh}(\text{SCN})\cdot\text{NH}_2$, must be assigned to *benziminobutyl ester thiocyanate*, for it decomposes when warmed with water into *isobutyl benzoate* and ammonium thiocyanate, or when heated above its melting point, into *isobutyl thiocyanate* and *benzamide*. This salt is prepared by mixing cold aqueous solutions of *benziminobutyl ester hydrochloride* and *potassium thiocyanate*.

[With BAYARD BAYNES.]—Ethyl carbethoxythiocarbamate,
 $\text{CO}_2\text{Et}\cdot\text{NH}\cdot\text{CS}\cdot\text{OEt}$,

boils at 135° under 13 mm. pressure and melts at 44° . When heated on the steam-bath with phenylhydrazine, it yields *3-ethoxy-1-phenyl-5-triazolone*, $\text{NPh}\begin{array}{c} \text{CO}\cdot\text{NH} \\ \diagdown \quad \diagup \\ \text{N}=\text{C}\cdot\text{OEt} \end{array}$, which melts at $150\text{--}151^\circ$, and is converted into Pinner's urazole (Abstr., 1887, 1043) when boiled with strong hydrochloric acid.

Acetylphenylurethane, $\text{CO}_2\text{Et}\cdot\text{NPhAc}$, was obtained by boiling phenylurethane with acetic anhydride and acetyl chloride in succession; it yields no triazole when warmed with phenylhydrazine; acetylphenylhydrazine, melting at 128° , is obtained instead. Similarly, acetylphenylthiocarbamide (Hugershoff, this vol., i, 156) forms no triazole with phenylhydrazine; phenylthiocarbamide was obtained.

C. F. B.

Molecular Rearrangement of Thioncarbamic, Thioncarbanilic, and Thioncarbazinic Esters: β -Alkyl- α -diketotetrahydrothiazoles. By HENRY L. WHEELER and BAYARD BARNES (*Amer. Chem. J.*, 1900, 24, 60—82. Compare Abstr., 1899, i, 797).—It has been previously shown that when methyl thioncarbamate, $\text{H}_2\text{N}\cdot\text{CS}\cdot\text{OMe}$, is treated with methyl iodide, it is transformed into the isomeric thiolcarbamate, $\text{H}_2\text{N}\cdot\text{CO}\cdot\text{SMe}$. Further investigations have proved that this molecular rearrangement is characteristic of compounds of the general type $\text{HXN}\cdot\text{CS}\cdot\text{OR}$. Alkyl thioncarbanilates (where $\text{X}=\text{Ph}$) react less readily than the carbamates, but alkyl phenylthioncarbazinates (where $\text{X}=\text{NHPh}$) readily become transformed in the cold, yielding the phenylthiolcarbazinates described by Busch and Stern (Abstr., 1899, i, 956).

Ethyl phenylthioncarbazinate, $\text{NHPh}\cdot\text{NH}\cdot\text{CS}\cdot\text{OEt}$, obtained together with an oily hydrazone by the action of phenylhydrazine on ethyl dithiocarbonate, crystallises from alcohol or light petroleum in needles melting at $72\text{--}74^\circ$, and when allowed to remain with an excess of methyl iodide, is transformed into methyl phenylthiolcarbazinate, with ethyl iodide into the ethyl thiolcarbazinate, and with benzyl chloride into benzyl phenylthiolcarbazinate. When the thioncarbazinate is treated with a 20 per cent. solution of phosgene in toluene, it is converted into *ethoxyphenylthiodiazolone*, $\text{NPh}-\text{N} \begin{array}{c} \diagup \quad \diagdown \\ \text{CO}\cdot\text{S}\cdot\text{C}\cdot\text{OEt} \end{array}$, which

crystallises from alcohol in colourless prisms melting at 38° . The sodium derivative of ethyl phenylthioncarbazinate forms a yellowish-

red powder, and when either this or the free ester is treated with benzoyl chloride, *ethyl α-benzoylphenylthioncarbazinate*, $\text{NPhBz} \cdot \text{NH} \cdot \text{CS} \cdot \text{OEt}$, melting at 173° is formed. *Methyl phenylthioncarbazinate* melts at 113° .

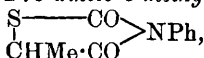
Diethyl thiocarbonate phenylhydrazone, $\text{NHPh} \cdot \text{N} \cdot \text{C}(\text{OEt}) \cdot \text{SEt}$, obtained as a bye-product in the preparation of ethyl phenylthioncarbazinate, or by the action of alcoholic potash and ethyl iodide on this ester, is a thick, yellowish-red oil which distils at $210\text{--}213^\circ$ under 36 mm. pressure, and on treatment with hydrogen sulphide at 125° for two hours, is converted back into the thion ester. When warmed for 12 hours on the water-bath with thiobenzoic acid, the products are ethyl phenylthiolcarbazinate and ethyl thiolbenzoate which distils at $252\text{--}253^\circ$ under 760 mm. pressure. *Ethyl α-benzoylphenylthiolcarbazinate*, $\text{NPhBz} \cdot \text{NH} \cdot \text{CO} \cdot \text{SEt}$, obtained by treating the phenylhydrazone or ethyl phenylthiolcarbazinate with benzoyl chloride, forms lozenge-shaped crystals melting at $138\text{--}139^\circ$.

Methylthioncarbanilate melts at $95\text{--}96^\circ$ (compare Orndorff and Richmond, this vol., i, 156), and when treated with methyl iodide yields methyl thiolcarbanilate (Will, Abstr., 1882, 723); *isobutyl thioncarbanilate* melts at $77\text{--}78^\circ$ (Orndorff and Richmond, $80\cdot5^\circ$), and when heated with *isobutyl* iodide does not undergo isomerisation.

When ethyl thioncarbamate and chloroacetic acid are heated together at 100° , the products are thioglycollic acid, ethyl thiolcarbamate, cyanuric acid, and *carbaminothioglycollic acid*, $\text{NH}_2 \cdot \text{CO} \cdot \text{S} \cdot \text{CH}_2 \cdot \text{CO}_2\text{H}$, melting at $135\text{--}136^\circ$. *isoAmyl thioncarbamate* and chloroacetic acid yield 2:5-diketotetrahydrothiazole, which melts at $123\text{--}125^\circ$ and distils at $178\cdot5\text{--}179\cdot5^\circ$ under 19 mm. pressure. The *silver* derivative, when treated with methyl iodide, yields the 1-methyl ether, melting at $37\text{--}39^\circ$ and distilling at $131\text{--}132^\circ$ under 15 mm. pressure.

Ethyl thioncarbanilate and chloroacetic acid yield ethyl chloride, water, and 1-phenyl-2:5-diketotetrahydrothiazole (*Annalen*, 1881, 207, 137).

[With G. K. DUSTIN.]—Ethyl-α-bromopropionate and ethyl thioncarbanilate yield 1-phenyl-2:5-diketo-3-methyltetrahydrothiazole,



crystallising in colourless needles and melting at 103° . Ethyl thioncarbanilate and ethyl α-bromoisobutyrate yield *ethyl carbanilo-α-thioisobutyrate*, $\text{NHPh} \cdot \text{CO} \cdot \text{SC}(\text{CH}_3)_2 \cdot \text{CO}_2\text{Et}$, crystallising in colourless prisms or pyramids, and melting at $79\text{--}81^\circ$.

[With LEEDS MITCHELL, G. K. DUSTIN, HARRY LE B. GRAY, HENRY A. NORTH and W. H. BUELL.]—α-Thiocyno-derivatives of the fatty esters are readily obtained by boiling the corresponding α-halogen fatty esters with potassium thiocyanate. They are oils with a penetrating, disagreeable odour, can be distilled under reduced pressure, and when treated with hydrochloric acid—more especially the methyl esters—undergo a transformation similar to that observed by Heintz (*Annalen*, 1865, 136, 22), and Claeson (*Ber.*, 1877, 10, 1352), yielding homologues of 2:5-diketotetrahydrothiazole. The following are the boiling points of the esters prepared:

α-Thiocyanoacetates: *methyl*, 120—122° (16 mm.); *ethyl*, 118—122° (15 mm.); *isoamyl*, 145—147° (17 mm.); *α*-thiocyanopropionates: *methyl*, 104—106° (15—16 mm.); *ethyl*, 107—108° (16 mm.); *isobutyl*, 130—131° (15 mm.); *isoamyl*, 141·5° (15 mm.); *α*-thiocyanoisobutyrate: *methyl*, 101—102° (17 mm.); *ethyl*, 111—115° (22 mm.); *isobutyl*, 132—133° (21 mm.); *isoamyl*, 135·5—136·5° (16 mm.); *α*-thiocyanobutyrate: *methyl*, 125° (23 mm.); *ethyl*, 134—136° (28 mm.); *isoamyl*, 158—160° (23 mm.); *α*-thioisovalerate: *methyl*, 119—121·5° (23 mm.); *ethyl*, 126—128° (19 mm.); *isobutyl*, 145—147° (19 mm.); *isoamyl*, 151—152° (14 mm.).

3-*Methyl*-2:5-diketotetrahydrothiazole, forms colourless plates melting at 46—47° and distilling at 165—168° under 20 mm. pressure. 3-*Dimethyl*-2:5-diketotetrahydrothiazole crystallises from water in extremely long, coloured prisms melting at 79—80°. 3-*Ethyl*-2:5-diketotetrahydrothiazole crystallises in six-sided prisms melting at 63—65°.

J. J. S.

Action of Diazobenzene on Nitromethane. By EUGEN BAMBERGER, OTTO SCHMIDT, and HERBERT LEVINSTEIN (*Ber.*, 1900, 33, 2043—2061).—Diazobenzene salts have no action on nitromethane; they react with isonitromethane under varying conditions in two ways, (i) to form phenylazoisnitromethane (nitroformaldehydephenylhydrazone), which by the further action of diazobenzene may be converted into nitroformazyl or phenylnitroformaldehydephenylhydrazone and (ii) to form phenylisonitromethane (phenylnitromethane), which by the further action of diazobenzene yields diphenylnitromethane or phenylazodiphenylnitromethane; in addition, phenylformazyl and benzaldehyde, benzophenonoxime and benzophenone, which are decomposition products of isonitro-compounds, two undetermined neutral compounds melting respectively at 105—106° and at 132° and an undetermined basic compound melting at 145° were isolated from the products of the reaction.

R. H. P.

Formation of a Nitrosoamine by the Action of Nitrous Acid on a Primary Aromatic Amine. By ERNST TAUBER and FRANZ WALDER (*Ber.*, 1900, 33, 2116—2118).—When, in the preparation of Bismarck brown, a cooled solution of sodium nitrite (1 mol.) is rapidly added to a cooled solution of *m*-phenylenediamine (1 mol.) in hydrochloric acid (2 mols.), as much as 20 per cent. of the diamine can be obtained in the form of a nitroso-derivative. Nitroso-*m*-phenylenediamine crystallises in red, monoclinic plates or needles, and its hydrochloride in reddish-brown to black needles. It melts and decomposes at 210°, is reduced in acid solution to 1:2:4-triaminobenzene, yields ammonia and a nitrosoaminophenol when boiled with aqueous sodium hydroxide, and does not give Liebermann's nitrosoamine reaction.

C. F. B.

Diazonium Hydroxides and Diazohydroxides. By ADALBERT ENGLER and ARTHUR HANTZSCH (*Ber.*, 1900, 33, 2147—2158. Compare Davidson and Hantzsch, *Abstr.*, 1899, ii, 6).—Many of the diazonium hydroxides are very strong bases. The dissociation constants were determined from the conductivity at 0° of dilute mixtures of the diazonium chloride with pure sodium hydroxide in molecular proportion. Anisole diazonium

hydroxide, $\text{OMe} \cdot \text{C}_6\text{H}_4 \cdot \text{N}_2 \cdot \text{OH}$, and pseudocumenediazonium hydroxide $\text{C}_6\text{H}_2\text{Me}_3 \cdot \text{N}_2 \cdot \text{OH}$, are bases equal in strength to the alkali hydroxides and the dissociation constants were too great to be determined. *p*-Bromobenzenediazonium hydroxide K 0.0149, 2:4-dibromobenzenediazonium hydroxide K 0.0136, and 2:4:6-tribromobenzenediazonium hydroxide K 0.0014, the strength of the base diminishing as the number of negative radicles increases. The undissociated part does not consist of true diazonium hydroxide, but of the *syndiazohydroxide* which forms the "pseudo-base," although no time-change can here be observed. Since *p*-bromobenzenediazonium hydroxide is much less dissociated than benzenediazonium hydroxide, its solution should contain more of the *syndiazohydroxide*, and it has been found that the conversion into a *syndiazotate* is virtually complete in presence of $2\frac{1}{2}$ mols. of sodium hydroxide, whereas benzenediazonium hydroxide requires a large excess of alkali. *p*-Nitrobenzenediazonium hydroxide is too unstable for accurate conductivity measurements, but was found to be a stronger base than ammonia.

The normal (*syn*) diazohydroxides are converted immediately into diazonium chlorides on adding 1 mol. of hydrochloric acid and no 'gradual neutralisation' phenomena could be detected by means of conductivity measurements even at 0° in the case of *p*-bromobenzenediazohydroxide. 'Gradual neutralisation' occurs, however, in the case of the *isodiazohydroxides*, which exist chiefly in the form of nitrosoamines as pseudo-bases, and the conductivity of a mixture of *p*-nitrophenylnitrosoamine and hydrochloric acid only became constant after about $3\frac{1}{2}$ hours at 0° .

T. M. L.

*syn*Diazotates. By ARTHUR HANTZSCH (*Ber.*, 1900, 33, 2158—2161).—On adding a solution of anisole diazonium bromide to 10 mols. of potassium hydroxide dissolved in an equal weight of water and cooled to -10° , *potassium anisolesyndiazotate*, $\text{OMe} \cdot \text{C}_6\text{H}_4 \cdot \text{N}_2 \cdot \text{OK}$, separates as a mass of colourless flakes, which liquefies immediately in moist air, dissolves unchanged in water at 0° , decomposes in solution at the ordinary temperature, but can be crystallised unchanged from concentrated potassium hydroxide solution.

Potassium pseudocumenesyndiazotate, $\text{C}_6\text{H}_2\text{Me}_3 \cdot \text{N}_2 \cdot \text{OK}$, was prepared in a similar manner, but was found to be much less stable.

T. M. L.

*syn*Diazocyanides and Diazonium Cyanides. By ARTHUR HANTZSCH (*Ber.*, 1900, 33, 2161—2179).—The diazocyanides resemble the hydroxides (Engler and Hantzsch, this vol., i, 566) in that the dissociated portion is in the form of a diazonium cyanide, $\text{R} \cdot \text{N}(\text{CN}) : \text{N}$, a true salt closely resembling potassium cyanide, whilst the undissociated portion is a 'pseudo-salt,' $\text{R} \cdot \text{N} : \text{N} \cdot \text{CN}$, resembling the azo-compounds.

Anisolesyndiazocyanide, $\text{OMe} \cdot \text{C}_6\text{H}_4 \cdot \text{N} : \text{N} \cdot \text{CN}$, is precipitated by alcoholic potassium cyanide from a cold solution of the diazonium chloride as an orange-red powder melting at 50 — 51° , and passes in about 30 hours into the *antidiazocyanide*, which crystallises from light petroleum in brownish-red needles, melts at 121 — 122° , and neither condenses with β -naphthol nor liberates nitrogen in contact

with copper powder. The *syndiazocyanide* dissolves unchanged in alcohol to a strongly-coloured, non-conducting solution; the aqueous solution, however, consists chiefly of *anisolediazonium cyanide*, $\text{OMe}\cdot\text{C}_6\text{H}_4\cdot\text{N}(\text{CN})\text{:N}$, is only slightly coloured, and has μ_{256}^{512} 49.6, $\mu_{512}^{53.9}$.

Pseudocumenediazocyanide, like the preceding compound, is a 'pseudo-salt' resembling the azo-compounds when in the solid state or in alcoholic solution, but in aqueous solution consists chiefly of *pseudocumenediazonium cyanide*, which gives $\mu_{512}^{50.6}$ at 0° , and is a true salt like the diazonium chloride.

2:4-Dibromobenzenediazocyanide, unlike the two preceding compounds, is only very slightly dissociated in dilute aqueous solution. Tribromobenzenes*syndiazocyanide* shows no tendency to form a diazonium cyanide, is indifferent to hydrochloric acid, but immediately precipitates silver cyanide from alcoholic silver nitrate. *p*-Bromobenzenediazocyanide in aqueous solution is about half dissociated to the diazonium cyanide, whilst solutions of *p*-chlorobenzenediazocyanide conduct somewhat less; diazobenzene cyanide itself is rather more than half dissociated to the diazonium cyanide.

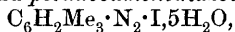
T. M. L.

*anti*Diazonaphthalene Salts and Naphthylnitrosoamine. By ADALBERT ENGLER (*Ber.*, 1900, 33, 2188—2190).—Sodium *antidiazonaphthalene*, $\text{C}_{10}\text{H}_7\cdot\text{N:N}\cdot\text{ONa}\cdot\text{H}_2\text{O}$, rapidly turns brown, dissolves in water to a colourless solution, has $\mu_{32}^{34.4}$, $\mu_{1024}^{38.0}$, and thus is not appreciably hydrolysed; it is therefore a salt of a true acid. On adding acetic acid, however, the compound which is liberated is not acid to litmus, only very slightly soluble in water, and a non-electrolyte; it is therefore regarded as the 'pseudo-acid' *naphthyl-nitrosoamine*, $\text{C}_{10}\text{H}_7\cdot\text{NH}\cdot\text{NO}$, and this view is confirmed by the fact that when dissolved in benzene it does not interact with phosphorus pentachloride, acetyl chloride, or ammonia.

T. M. L.

Nature of the Diazohaloids. By ARTHUR HANTZSCH (*Ber.*, 1900, 33, 2179—2188).—Except in certain cases where the diazonium ion is coloured, the coloured explosive diazohaloids are regarded as consisting chiefly of the true azo-compound $\text{R}\cdot\text{N:NCl}$, whilst the colourless diazohaloids, which are much less explosive, are regarded as diazonium haloids, $\text{R}\cdot\text{NCl:N}$; coloured nitrates and sulphates only occur when the diazonium ion is coloured.

Mesitylenediaziodide, $\text{C}_6\text{H}_2\text{Me}_3\cdot\text{N}_2\cdot\text{I} + 6$ or $7\text{H}_2\text{O}$, crystallising in golden-yellow needles, and *pseudocumenediaziodide*,



remain constant in weight at -5° , effloresce at 0° , and then decompose. *Anisole diaziodide*, $\text{OMe}\cdot\text{C}_6\text{H}_4\cdot\text{N}_2\cdot\text{I}$, forms golden-yellow needles, and is somewhat more stable than the preceding compounds, but explodes when rubbed.

The remaining diaziodides in which the diazonium hydroxide is a weaker base (see Engler and Hantzsch, this vol., i, 566) are much less stable and could not be isolated.

All the diazochlorides are colourless and not more explosive than the colourless nitrates; the yellow colour of naphthalenediazochloride is perhaps due to decomposition products. The diazobromides are

almost all coloured and explosive; pseudocumenediazobromide, at the moment of precipitation, and *p*-thiocyanobenzene diazobromide, $\text{SCN}\cdot\text{C}_6\text{H}_4\cdot\text{N}_2\cdot\text{Br}$, are colourless; anisole diazobromide has only a slight greenish-yellow tint. The diaziodides are still more coloured and explosive, whilst the diazothiocyanates are intermediate between the bromides and iodides. The diazocyanides (see this vol., i, 567) form the other limiting case, and are exclusively azo-compounds when in the solid state.

T. M. L.

Hydrazones and Osazones from *p*-Nitrophenylhydrazine. By FRANZ FEIST (*Ber.*, 1900, 33, 2098—2099).—*Furfuraldehyde-p-nitrophenylhydrazone* is a bright red substance which crystallises from alcohol, melts at 127° , and dissolves in sodium hydroxide, forming a reddish-violet solution. *1-Methylfurfuraldehyde-p-nitrophenylhydrazone* is a ruby-red powder which melts at 130° and dissolves in dilute sodium hydroxide, forming a cherry-red solution. *Lævulinic acid p-nitrophenylhydrazone* crystallises in small, lustrous needles which melt at 174 — 175° and dissolves in sodium hydroxide, forming a deep red solution. *p-Nitrophenylrhannosazone* crystallises in microscopic, vermilion-coloured needles which melt and froth at 208° and dissolve in sodium hydroxide, forming a deep blue solution.

R. H. P.

Action of Chloroacetic Acid and Chloroacetone on Thiocarb-anilides and Thiosemicarbazides. By REINHOLD VON WALTHER and A. STENZ (*J. pr. Chem.*, 1900, [ii], 61, 575—576).—Thiocarb-anilide reacts with *p*-toluidine to form phenyl-*p*-tolylthiocarbamide; if the reaction takes place in alcoholic solution, the product melts at 158° , but if in glacial acetic acid solution it melts at 141° , and is convertible into the isomeride melting at 158° . Phenyl-*p*-tolylthiosemicarbazide has been obtained in two forms, which melt respectively at 165° and 176° , and phenyl-*p*-tolylthiohydantoin has also been obtained in two forms, which melt at 169° and 113° . Chloroacetic acid reacts with diphenylthiosemicarbazide (m. p. 165°), forming two isomeric compounds, of which one melts at 200° and by the action of alcoholic hydrochloric acid can be converted in the second melting at 210° ; phenyl-*p*-tolylthiocarbamide reacts with chloroacetone to form two thiazolines melting at 116° and 136° respectively. This isomerism is not yet explained.

R. H. P.

Coloured Rosaniline Bases and their Colouring Properties. By GEORG VON GEORGIEVICS (*Monatsh.*, 1900, 21, 407—412).—A continuation of the controversy between the author and Weil (compare Abstr., 1896, i, 565). The red colour which the carbinol base gradually assumes and the coloration on filter paper produced by an ethereal solution of rosaniline can be explained by the formation of a "rosaniline rosanilate" by the combination of the rosaniline ammonium base (rosanilinium, compare Hantzsch and Osswald, this vol., i, 256) with the carbinol base, which acts as an acid in the presence of strong bases.

R. H. P.

Preparation of Phosphoryl Derivatives of Aromatic Amines. By WILHELM AUTENRIETH and P. RUDOLPH (*Ber.*, 1900, **33**, 2099—2111).—The amine NH_2R is emulsified by shaking with slightly more than the calculated quantity of 10—25 per cent. aqueous sodium hydroxide, or 30—40 per cent. aqueous sodium carbonate, and about three times the theoretical amount of phosphorus oxychloride is added, the shaking being continued and the mixture kept cool with ice. The substituted amide, $\text{PO}(\text{NHR})_3$, separates; in solution, there remains a substituted amino-acid, $\text{OH}\cdot\text{PO}(\text{NHR})_2$, which can be precipitated by the addition of a dilute mineral acid. The phosphoramides crystallise well; they can be brominated and nitrated; they are stable in cold water and aqueous acids and alkalis, and even in boiling alcoholic potash, but are hydrolysed when heated with strong hydrochloric acid under pressure. The aminophosphoric acids are less easy to obtain crystalline, and are rather less stable; when their dry sodium salts are rubbed with phosphorus pentachloride, the chlorides, $\text{Cl}\cdot\text{PO}(\text{NHR})_2$, are formed; these are crystalline and stable in cold water.

The amines experimented with were aniline, *o*- and *p*-toluidine, *p*-chloroaniline, and *p*-phenetidine. Of the compounds obtained those which are new are enumerated below, with their melting points. Dianilinoorthophosphoric acid, 214—216°; *dianilinophosphoryl chloride*, $\text{Cl}\cdot\text{PO}(\text{NHPh})_2$, 159°. *Phosphorylbromotoluidide*, $\text{PO}(\text{NH}\cdot\text{C}_6\text{H}_3\text{MeBr})_2$, 222°; *di-p-toluinophosphoric acid*, 195° (not 124°; compare Rudert, *Abstr.*, 1893, i, 324). *Phosphoryl-p-chloroanilide*, $\text{PO}(\text{NH}\cdot\text{C}_6\text{H}_4\text{Cl})_3$, 248—250°; *di-p-chloroanilinophosphoric acid*, $\text{OH}\cdot\text{P}(\text{NH}\cdot\text{C}_6\text{H}_4\text{Cl})_2$, 218°. *Phosphoryl-p-phenetidine*, $\text{PO}(\text{NH}\cdot\text{C}_6\text{H}_4\cdot\text{OEt})_3$, 168°; *nitro-derivative*, $\text{PO}[\text{NH}\cdot\text{C}_6\text{H}_3(\text{NO}_2)\cdot\text{OEt}]_3$, yellow, 126°; *di-p-phenetidino phosphoric acid*, $\text{OH}\cdot\text{PO}(\text{NH}\cdot\text{C}_6\text{H}_4\cdot\text{OEt})_2$, 202°.

[W. AUTENRIETH and O. HILDEBRAND.]—Phenylmercaptan can be converted into phosphate by treatment in alkaline solution with phosphorus oxychloride, just as the phenols can. The product, phenyl trithiophosphate, $\text{PO}(\text{SPh})_3$, melts at 114° (not 72°).

C. F. B.

Action of Phosphorus Thiochloride on Aromatic Amines in the Presence of Alkali. By WILHELM AUTENRIETH and P. RUDOLPH (*Ber.*, 1900, **33**, 2112—2115).—The action of phosphorus thiochloride is similar to that of the oxychloride (preceding abstract), except that the amide is here always the main product of the reaction, and the amino-acids are less stable, and in consequence were not isolated in the pure state. A 10 per cent. sodium hydroxide solution was used, and the phosphorus thiochloride was employed in about twice the calculated amount.

The following are the new compounds prepared, with their melting points. *Thiophosphorylanilide*, $\text{PS}(\text{NHPh})_3$, 153—154°, identical with the supposed $\text{PS}(\text{C}_6\text{H}_4\cdot\text{NH}_2)_3$ of Knop (*Abstr.*, 1888, 265), but not with the probably impure compound of Chevrier (*Zeit. Chem.*, 11, 539). *Thiophosphoryl-p-phenetidine*, $\text{PS}(\text{NH}\cdot\text{C}_6\text{H}_4\cdot\text{OEt})_3$, 152°. Thiophosphoryl-*p*-toluidide was also prepared.

C. F. B.

Metallic Derivatives of Diazoaminobenzene. By LOUIS MEUNIER (*Compt. rend.*, 1900, 131, 50—53).—The cuprous derivative of diazoaminobenzene is conveniently prepared, either by heating a benzene solution of the base with cuprous oxide, or by digesting its warm alcoholic solution with ammoniacal cuprous chloride. The compound is thus obtained in reddish-yellow leaflets decomposing at 270° ; when hydrogen sulphide is passed into its benzene solution, cuprous sulphide is precipitated, whilst diazoaminobenzene remains dissolved; it is decomposed explosively by nitric acid at the ordinary temperature. The hydrochloride of the preceding compound, $(N_2Ph \cdot NCuPh)_2 \cdot 2HCl$, is obtained by the action of benzyl chloride on a benzene solution of the diazoamino-compound in the presence of copper powder; it consists of light yellow, microscopic needles insoluble in the ordinary solvents and decomposing at 180° . The hydrobromide and hydriodide are obtained in a similar manner.

The cupric derivative of diazoaminobenzene, produced by mixing together slightly alkaline alcoholic solutions of the latter and of copper nitrate, forms greenish-black needles, insoluble in alcohol and ether, but soluble in benzene; it melts and decomposes at 170° . It is quite possible that the inorganic cuprous and cupric ammonium compounds and the corresponding mercury salts have constitutions analogous to those of the copper derivatives of diazoaminobenzene.

G. T. M.

Acetophenoneazobilirubin. By FR. PRÖSCHER (*Zeit. physiol. Chem.*, 1900, 29, 411—415).—In 1883, Ehrlich in his work on the diazo-reaction in urine, showed that bilirubin forms a coloured product with diazobenzenesulphonic chloride. The present communication shows that bilirubin can form monoazo-derivatives also, for example, acetophenoneazobilirubin, $C_{24}H_{25}O_4N_4$, which crystallises in minute needles, black by transmitted, but magenta-coloured by reflected light. It gives characteristic absorption bands which are described fully.

W. D. H.

Hexon Bases: Lysine. By YANDELL HENDERSON (*Zeit. physiol. Chem.*, 1900, 29, 320—328).—Eight preparations of lysine from different sources were examined with a view to seeing whether there are several substances included under that name. The result shows that lysine is a single substance. From experiments in which lysine was fused with alkali, the constitution $NH_2 \cdot [CH_2]_4 \cdot CH(NH_2) \cdot CO_2H$ is assigned to it.

W. D. H.

Action of Heat, Dilute Acids, and Alcohol on Albuminin. By ALEXEI A. PANORMOFF (*J. Russ. Phys. Chem. Soc.*, 1900, 32, 249—252. Compare Abstr., 1899, i, 655, and this vol., i, 126, 127).—A compound of albuminin with hydrogen chloride having a constant composition is obtained as follows. A saturated aqueous solution of albuminin is dialysed into water during three days and to the filtered, dialysed solution 4 per cent. hydrochloric acid is added until the liquid is acid to tropæolin OO. The solution is immediately precipitated with a mixture of alcohol and ether and the precipitate washed with alcohol and pressed between filter paper. The substance thus obtained does

not dissolve in water, but only swells up and on heating on the water-bath yields a thick, opalescent solution which will not filter; on adding alcohol and ether, washing the precipitate first with alcohol and then with ether and drying in a current of air, a substance of the composition $\text{Alb}, 3\text{HCl}$, where $\text{Alb} = \text{C}_{144}\text{H}_{225}\text{O}_{50}\text{N}_{37}\text{S}_2$, is obtained. The action of 0.1 per cent. hydrobromic acid on albumin gives the compound $2\text{Alb}, 5\text{HBr}$, whilst dialysis of a solution in 0.2 per cent. phosphoric acid yields the compound $\text{Alb}, 2\text{H}_3\text{PO}_4$. Separate portions of a filtered, dialysed, saturated, aqueous solution of albumin were treated as follows: (1) evaporated in a vacuum; (2) precipitated with methyl alcohol and repeatedly washed with the boiling alcohol; (3) precipitated and washed with ethyl alcohol; (4) precipitated by boiling in a sealed tube. All the precipitates on drying at 100° gave on analysis the composition $\text{C}_{144}\text{H}_{225}\text{O}_{50}\text{N}_{37}\text{S}_2$, but only that treated as in (1) was soluble in water at the ordinary temperature. T. H. P.

Effect of Desiccation of Albumin on its Coagulability. By J. BRET LAND FARMER (*Proc. Roy. Soc.*, 1900, **66**, 329—333).—The temperature at which aqueous solutions of albumin coagulate is not constant even for the same type of albumin. Whilst solutions of albumin from freshly-laid hens' eggs became opalescent at as low as 60° and coagulated at 64° , another sample showed opalescence at 65.5° and coagulated at 68° .

The dried egg albumin employed in the experiments now described dissolved readily in water; the filtered solution became opalescent at 60° and coagulated at 62 — 63° . When the substance was heated alone for 2—3 hours at 80° , it became insoluble; if, however, it is carefully dried at 52 — 55° , it may be afterwards kept for many hours at a temperature of 102 — 110° without undergoing any change, so far as could be observed. When dissolved in water and gradually heated, the solution became opalescent, and coagulated at the same temperatures as before desiccation.

N. H. J. M.

Invertin. By MARTIN KÖLLE (*Zeit. physiol. Chem.*, 1900, **29**, 429—436).—Osborne showed that his preparation of invertin yielded on decomposition a sugar the nature of which was not determined. It is now shown by the examination of the osazone that the sugar in question is mannose. W. D. H.

Preparation of Thymin. By WALTER JONES (*Zeit. physiol. Chem.*, 1900, **29**, 461—466).—The want of knowledge of the constitution of thymin is largely due to the difficulty of obtaining the pure substance from nucleic acid. The method now introduced avoids this by operating directly on herring roe with sulphuric acid; the product is subsequently treated with baryta water, and the thymin ultimately obtained as a silver compound, the solubility of which enables it to be easily separated from other silver salts formed. The method is described in full detail. W. D. H.

Preparation of Nucleic Acids. By P. A. LEVENE (*J. Amer. Chem. Soc.*, 1900, **22**, 329—331).—The methods of preparation of nucleic acid which involve heating with alkalis are objectionable,

since they change to some extent the original character of the substance. The following method yields satisfactory results. The nucleoprotein material is digested with solution of sodium hydroxide (5 per cent.) or ammonia (8 per cent.) for 2 hours in a cool place; acetic acid is then gradually added until the solution is only slightly alkaline. The mixture is now neutralised with picric acid in order to remove the proteids, and then rendered strongly acid by the addition of more acetic acid; it is left for some time, filtered, and alcohol added until the whole of the nucleic acid is precipitated. The author has applied this method to the preparation of nucleic acids from ovovitellin, ichtulin of cod-fish eggs, cod-fish sperm, pancreas, and *Bacillus tuberculosis*. E. G.

Nucleic Acid of the Embryo of Wheat and its Protein Compounds. By THOMAS BURR OSBORNE and GEORGE F. CAMPBELL (*J. Amer. Chem. Soc.*, 1900, 22, 379—413).—This paper contains an account in detail of the examination of wheat germs freed from bran and endosperm and ground into meal. This was separated into the following substances (the numbers indicate the percentage of the total nitrogen obtained in the form of each constituent): Insoluble in water and salt solution, 30; globulin (insoluble in water, soluble in salt solution), 19; albumin (soluble in water, coagulable by heat), 30; proteose (soluble in water, not coagulable by heat, precipitated by tannin), 9; (not precipitated by tannin), 11. The globulin and albumin yield a nuclein when digested with pepsin. The nuclein can be precipitated in two parts by dissolving it in dilute alkali and adding, first a slight excess of dilute hydrochloric acid, and then strong hydrochloric acid in considerable quantity to the filtrate from the first precipitate. The first precipitate consists of a protein, the second of a *nucleic acid* with a composition (corrected for ash, as are also the other results quoted) corresponding with that required for the formula $C_{21}H_{31}O_{15}N_8P_2$. This acid differs from any nucleic acid hitherto described; when hydrolysed with hot 2 per cent. hydrochloric acid, it yields guanine, adenine, phosphoric acid, and other products, but no sugar.

If it be assumed that the albumin, globulin, and nuclein are compounds of this nucleic acid with substances free from phosphorus, the amount of nucleic acid in each compound can be calculated from the percentage of phosphorus found therein, and by subtracting the amounts of carbon, hydrogen, oxygen, and nitrogen contained in this amount of nucleic acid from the amounts found in the analysis of the globulin, &c., the composition of the other constituent containing no phosphorus can be ascertained. This constituent is to be regarded as the true *protein*, and should alone be designated *albumin*, &c.; it is to be regarded as a poly-acid base (compare Abstr., 1899, i, 836), and the substances of varying composition, actually obtained, as compounds of this base with an acid in varying proportions; the acid being nucleic acid in the present case, the "albumins" in question should be called *nucleoalbumins*. The protein constituents of the nucleins were actually found to have compositions very similar to those of the protein constituents

in the albumin or globulin from which they were derived respectively. Thus, no special distinction can be made between nucleins and nucleoproteids; the former simply contain a relatively greater amount of nucleic acid. The insoluble portion of the wheat germs is probably composed also of a protein and nucleic acid. Probably the substances described do not exist as such in the germs, but are formed, or at least altered in composition, during the manipulation; it seems, generally speaking, that the more insoluble forms contain the larger proportion of nucleic acid. The proteids of the embryo undergo these changes more readily than do those of the dormant endosperm.

The albumin, or better nucleoalbumin, was obtained in yield equal to 10 per cent. of the embryo. It coagulates partially at 52—65°; at 100°, about 1/3 more coagulates. It is identical with the leucosin of wheat, rye, barley, and malt (Abstr., 1896, i, 399, 455, 714). The globulin, or better nucleoglobulin, was obtained in 5 per cent. yield; it coagulates at 87—90° when dissolved in 10 per cent. aqueous sodium chloride. The proteose was separated by salting-out into two parts, one insoluble, the other soluble, in saturated salt solution.

The composition of the substances obtained is given below; in most cases, the number quoted is the mean of several results.

	C.	H.	O (diff.).	N.	S.	P.
Nucleic acid.....	36.48	4.48	33.91	16.17	—	8.96
Leucosin*.....	52.65	7.04	22.56	16.43	1.32	—
Globulin*	51.57	7.07	22.11	18.60	0.65	—
Proteose..... {	insol.	49.94	6.80	24.94	17.08	1.24
	sol....	48.65	6.75	26.82	16.68	1.10

* After subtracting the nucleic acid.

C. F. B.

Protein Constituents of Egg White. By THOMAS BURR OSBORNE and GEORGE F. CAMPBELL (*J. Amer. Chem. Soc.*, 1900, 22, 422—450. Compare Abstr., 1899, i, 836).—A large quantity of white of egg was subjected to fractional precipitation with ammonium sulphate; 6 litres from 240 eggs yielded 500 grams of protein substances, and of these 280 grams were separated in crystalline form. The substance, hitherto regarded as globulin, which is precipitated by diluting white of egg, is nearly all ovomucin (Eichholz, Abstr., 1898, ii, 541), and forms about 7 per cent. of the proteid matter. It coagulates in aqueous sodium chloride solution at 75—78°, and does not dissolve in 1 per cent. sodium carbonate solution.

The substance precipitated in the crystalline form by ammonium sulphate is ovalbumin; this portion forms 50 per cent. of the proteid matter, and more ovalbumin is contained in the other fractions, so that it is the chief constituent of white of egg. The influence of concentration on the coagulation was studied, and also that of sodium chloride and of hydrochloric and acetic acids; the point of coagulation falls slightly with increasing concentration of the ovalbumin, but rises with increasing percentage of sodium chloride. The specific rotation, $[\alpha]_D$, was -28.60° to -30.80° in different fractions. The carbo-

hydrate, which was eliminated from ovalbumin by boiling the latter with 3 per cent. hydrochloric acid for $\frac{1}{2}$ hour, yielded a phenylosazone which melted at 187—189°, and had not quite the same appearance as phenylglucosazone. It is thought to be derived undoubtedly from the ovalbumin, and not from any ovomucoid present as an impurity. Its amount is probably 3—5 per cent. of the ovalbumin.

The fractions remaining after separation of the ovalbumin in the crystalline form yield, at 65°, a coagulum of *conalbumin*; at 90°, another coagulum containing ovalbumin, conalbumin, and ovomucoid, whilst ovomucoid remains in solution. Conalbumin resembles ovalbumin in properties and composition; hence its name. From solutions in 10 per cent. aqueous sodium chloride it coagulates at 55—60°; in aqueous solution only, it is not completely coagulated before the ovalbumin begins to separate. The specific rotation was determined in 10 per cent. aqueous sodium chloride solution containing also ovalbumin and ovomucoid; allowing for the rotation due to these, it was found to be $[\alpha]_D - 36^\circ$ to -39° .

Ovomucoid was found to have the specific rotation $-61^\circ 10'$ to $-61^\circ 38'$.

The composition of the four substances was:

	C.	H.	O (diff.).	N.	S.	P.
Ovomucin.....	50.82	6.88	25.64	14.66	1.94—2.28	—
Ovalbumin....	52.75	7.10	22.90	15.51	1.62	0.12
Conalbumin...	52.25	6.99	22.95	16.11	1.70	—
Ovomucoid...	48.96	6.53	29.71	12.44	2.36	—

C. F. B.

Schinoxydase, an Oxydase present in Schinus Molle. By J. SARTHOU (*J. Pharm.*, 1900, [vi], 11, 482—488).—The latex of *Schinus molle* is a milky fluid which on exposure to the air becomes bluish in colour, and finally brown. This colour change is effected by an enzyme, *schinoxydase*, which is capable of rapidly bringing about the oxidation of quinol, resorcinol, pyrogallol, and potassium ferrocyanide, by means of atmospheric oxygen, and is hence an aeroxidase. The enzyme can be isolated by precipitating an emulsion of the latex formed with water by means of alcohol of 95° sufficiently large in amount to dissolve the resin present; it is obtained as a white, flocculent precipitate, which is easily soluble in water; the aqueous solution acts as an oxidising agent with the substances named. When the oxydase is dehydrated, either by leaving it in contact for several minutes with alcohol of 95°, or in a vacuum, it temporarily loses its oxidising power, although this is immediately restored on rehydration; on the other hand, the enzyme, when left for 24 hours in contact with alcohol, loses its flocculent appearance and becomes coagulated, whilst its properties as an oxydase are permanently destroyed.

W. A. D.

Function of Iron in Schinoxydase. By J. SARTHOU (*J. Pharm.*, 1900, [vi], 11, 583—589. Compare preceding abstract).—The ash of schinoxydase contains a considerable quantity of iron, calcium, and

sodium, but no manganese; since the oxidising power of the latex of *Schinus molle* is nearly proportional to the amount of iron it contains, the author considers that iron plays the same part in schinoxydase in promoting oxidation as manganese in Bertrand's laccase.

The action of a number of ferrous salts in promoting the oxidation of easily oxidisable substances by atmospheric oxygen is dealt with, and the following conclusions may be drawn. (1) That iron, in the form of salts of carboxylic acids, is only slightly capable of promoting oxidation, but is very active in the form of ferrous cyanide and ferrous ammonium sulphate, although slightly less rapid with the latter than with the former. (2) Ferrous hydroxide, washed free from alkali, is also very active; it is noteworthy that the amount of oxygen absorbed by the hydroxide in presence of quinol is much greater than that which is absorbed, under similar conditions, by the ferrous hydroxide alone, although the quinol alone is non-absorbent. (3) Finally, for the same quantity of iron, the amount of oxygen rendered active depends on the state of combination of the iron. W. A. D.

Proteolytic Diastase of Malt. By AUG. FERNBACH and L. HUBERT (*Compt. rend.*, 1900, 130, 1783—1785).—The coagulable albumin of filtered malt extract, prepared at the ordinary temperature, becomes non-coagulable when the solution is digested at temperatures below 70°. This change is not due to microbes, for a similar result is obtained in media sterilised by means of a Chamberland filter, neither is it brought about by the dissolved salts, for the action is prevented by warming the solution. The cold sterilised extract renders gelatin soluble, whereas the heated solution has no effect on this substance. These results point to the presence of a proteolytic diastase in the malt extract. By treating the solution with alcohol, a precipitate is obtained which has a solvent action on the coagulable albumin of malt extract, and also on the insoluble nitrogenous compounds of the barley grain. This action commences at 40°, reaches its maximum at 60°, and is still very marked at 70°.

The nature of the soluble products formed from the malt proteids during brewing by the proteolytic diastase, varies with the temperature of digestion. On applying the phosphotungstic acid test, it is found that at 40° the soluble nitrogen is wholly present in amino-compounds, whilst at 60° and 70° the aminic nitrogen forms only 50—60 and 40 per cent. respectively of the total quantity of this element present in solution. G. T. M.

Organic Chemistry.

Configuration and Classification of Aliphatic Compounds. By FRIEDRICH KRAFFT (*J. pr. Chem.*, 1900, [ii], 62, 75—82. Compare Petrenko-Kritschenko, this vol., i, 421).—An account is given of the gradual disappearance of the line of separation between the fatty and aromatic compounds. The special properties of the carbon atom in both series of compounds is regarded as depending, not only on its quadrivalency, but also on the fact that it has the smallest atomic volume of all the elements.
T. M. L.

Hydrocarbons in Heavy Texas Petroleum. By CHARLES F. MABERY and D. M. BUCK (*J. Amer. Chem. Soc.*, 1900, 22, 553—556).—The crude oil examined was thick and of a dark colour; it contained 0.94 per cent. of sulphur and appreciable quantities of water, and had a sp. gr. 0.950 at 20°. By the aid of fractional distillation under diminished pressure, and removal of benzene hydrocarbons by fuming sulphuric acid, the following compounds have been isolated: $C_{14}H_{26}$, 125—130°, sp. gr. 0.8711; $C_{15}H_{28}$, 140—145°, sp. gr. 0.8788; $C_{16}H_{30}$, 160—165°, sp. gr. 0.8894; $C_{17}H_{34}$, 175—180°, sp. gr. 0.8966; $C_{19}H_{36}$, 195—200°, sp. gr. 0.902; $C_{21}H_{38}$, 215—220°, sp. gr. 0.9163; $C_{25}H_{46}$, 270—275°, sp. gr. 0.941. The boiling points given are all under a pressure of 25 mm.

In order to avoid decomposition of the higher fractions, they were first mixed with light petroleum before treatment with fuming sulphuric acid.
J. J. S.

Norwegian Tar. By KNUT T. STRÖM (*Bied. Centr.*, 1900, 29, 574—575; from *Kristiania Videnskabs-Selskabs Verhandl.*, 1899).—The tar was obtained by burning pine-wood in holes in the ground. It contained 4.75 per cent. of acids (as acetic acid), 10.94 per cent. of phenols, and 60.80 per cent. of hydrocarbons and other indifferent substances. Sp. gr. 1.068 at 15°. Formic, acetic, propionic, *n*-butyric, valeric, methylpropylacetic, *n*-caproic, cœnanthoic, *n*-caprylic, and possibly pelargonic, capric, and (inactive) pimelic acids, cresol guaiacol, ethyl- and propyl-guaiacol, a compound, $C_{11}H_{16}O_2$ (perhaps methylpropyl-guaiacol), in the fraction boiling at 260—265°, and a compound, $C_{12}H_{14}O_2$, in the distillate which boiled at over 300° were found.

The hydrocarbons and other indifferent substances (14 per cent. solid and 86 per cent. liquid) included retene and terpenes.

N. H. J. M.

General Method for the Preparation of Halogen Derivatives of Aliphatic Hydrocarbons. By ANTOINE MOUNEYRAT (*Ann. Chim. Phys.*, 1900, [vii], 20, 485—574).—A detailed account of work already published (*Abstr.*, 1898, i, 613, 625; 1899, i, 1, 97, 241, 247, 341, 397, 470, 555, 556, 725, 786).
W. A. D.

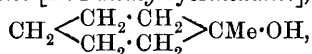
Electrolytic Syntheses of Organic Substances. II. (Iodoform.) By OCTAVE DONY-HENAU (Zeit. Elektrochem., 1900, 7, 57).—The discharge potential of iodine ions in a solution containing sodium

carbonate is not diminished by the presence of alcohol. The author concludes, therefore, that the formation of iodoform is not to be attributed to the direct action of iodine on alcohol. It is probably due to the action of hypoiodite, $\text{EtOH} + 5\text{HIO} = \text{CHI}_3 + \text{CO}_2 + 2\text{HI} + 4\text{H}_2\text{O}$, the small (and variable) quantity of iodate formed being due to the change $3\text{HIO} = \text{HIO}_3 + 2\text{HI}$. The author shows that the second change is retarded by the presence of either iodide or iodate, and that the yield of iodoform, from a given quantity of iodine, is therefore greater in presence of excess of these substances. He also shows that iodoform is produced by the action of a solution of hypoiodous acid (made by shaking together iodine, mercuric oxide, and water) on a solution of alcohol, potassium iodide, and sodium carbonate at 60° . That chloroform and bromoform cannot be made by the electrolytic method is due to the fact that the discharge potentials of chlorine and bromine are higher than that of hydroxyl. Oxidation products of alcohol are therefore produced instead of chloroform or bromoform. T. E.

New Method for the Preparation of Nitromethanes. By VICTOR AUGER (*Bull. Soc. Chim.*, 1900, [iii], 23, 333—336).—When potassium chloroacetate is heated with sodium nitrite in concentrated aqueous solution, carbon dioxide is evolved and nitromethane is formed. The author finds that many of the nitroparaffins may be obtained by means of this reaction, and details are given in the paper of the preparation of nitroethane from α -bromopropionic acid, nitropropane from α -bromobutyric acid, nitroisobutane from α -bromoisovaleric acid, and nitrohexane from α -bromoheptic acid. α -Bromoisobutyric acid and active valeric acid (methylthylacetic acid), when treated with sodium nitrite, yield isopropylpseudonitrole and β -butylpseudonitrole respectively. No definite products could be obtained from α -bromopalmitic acid. N. L.

Tertiary Derivatives of Heptanaphthene [Methylcyclohexane]. By WLADIMIR B. MARKOWNIKOFF and WLADIMIR TCHERDINTZEFF (*J. Russ. Phys. Chem. Soc.*, 1900, 32, 302—303).—[With EFIMOFF.]—tert.-Nitroheptanaphthene [1-nitro-1-methylcyclohexane], $\text{CH}_2 \begin{smallmatrix} \text{CH}_2 \cdot \text{CH}_2 \\ \text{CH}_2 \cdot \text{CH}_2 \end{smallmatrix} \text{CMe} \cdot \text{NO}_2$, is a liquid with an odour resembling that of turpentine; it boils at $109\text{--}110^\circ$ under 40 mm. pressure, has the sp. gr. 1.0367 at $0^\circ/0^\circ$ and 1.025 at $20^\circ/0^\circ$, and on cooling solidifies to a glassy mass melting at -71° . The corresponding amine, $\text{C}_7\text{H}_{15}\text{N}$, boils at 141° and solidifies to a vitreous mass melting at -96° ; the hydrochloride melts at $256\text{--}257^\circ$; the salts are in general readily soluble, but the sulphate, crystallising in plates, and the oxalate, in leaflets, are only slightly soluble; the platinichloride (with $1\text{H}_2\text{O}$) forms beautiful, brick-red octahedra and tetrahedra; the slightly soluble aurichloride separates in golden-yellow needles, and the auribromide in flat, dark brown needles.

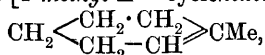
tert.-Heptanaphthenol [1:1-methylcyclohexanol],



obtained by diazotising the salts of the amine, boils with partial decomposition at 155° under 742 mm. pressure. It solidifies on cooling,

and melts at 12°. The corresponding *chloride*, $C_6H_{10}MeCl$, boils at 53—55° under 40 mm. and, under ordinary pressure, at 148—151° with decomposition.

α -(or 1:2)-*Naphthylene* [1-methyl- $\Delta^{1,2}$ -cyclohexene],



boils at 108° under 747 mm. pressure.

T. H. P.

Secondary Derivatives of Heptanaphthene [*Methylcyclohexane*]. By WLADIMIR B. MARKOWNIKOFF (*J. Russ. Phys. Chem. Soc.*, 1900, **32**, 303—305).—The physical constants of several secondary heptanaphthene derivatives, previously obtained by Wallach (*Abstr.*, 1896, i, 309) and Zelinsky (*Abstr.*, 1897, i, 462), have been revised.

β -Methylnaphthenol [1:3-*Methylcyclohexanol*] is a viscous liquid which boils undecomposed at 173·7—174° under 769 mm. pressure, and solidifies to a glassy mass melting at -47°; it has the sp. gr. 0·9286 at 0°/0°, and 0·9158 at 20°/0°, and the specific rotation $[\alpha]_D$ 3°44·1'; it dissolves in 97 volumes of water. The halogen derivatives of this naphthenol consist of mixtures of two isomerides. Thus the chloride under ordinary pressure decomposes into hydrogen chloride and the hydrocarbon C_7H_{12} , which boils at 156—159°; but on treating the chloride with alcoholic potash, the greater part is decomposed into the naphthylene boiling at 103°, whilst the remaining chloride boils undecomposed at 160—161°. The iodide, after the same treatment, boils at 200—205° without decomposition. The β -naphthylene (2:3) boils at 103° under 768 mm. pressure.

T. H. P.

Erythritol in Trentepohlia Jolithus. By MAX BAMBERGER and ANTON LANDSIEDL (*Monatsh.*, 1900, **21**, 571—573).—The alga *Trentepohlia Jolithus* (*Chroolepus Jolithus*), when extracted with ether, yields erythritol and a ruby-red, sticky mass, which is coloured an intense blue with concentrated sulphuric acid.

R. H. P

Some Phosphoric Esters. By JACQUES CAVALIER and EUGÈNE PROST (*Bull. Soc. Chim.*, 1900, [iii], **23**, 678—681. Compare this vol., i, 75).—*n*-Propyl, isopropyl, and isobutyl phosphates are analogous to the methyl and ethyl esters, and are obtained in a similar manner, the trialkyl phosphates by heating together mol. proportions of silver phosphate and alkyl iodide, and the mono- and di-alkyl phosphates by the action of phosphoric oxide on the alcohols, the separation of the latter esters being effected by means of their barium salts.

Tripropyl phosphate, $PO_4Pr^a_3$, is a colourless liquid which is slightly soluble in water, and boils without decomposition at 138° under 47 mm. pressure, and at 133·5° under 22 mm. pressure. *Lead dipropyl phosphate*, $(PO_4Pr^a_2)_2Pb$, crystallises in small, anhydrous needles melting at 145—147°; it decomposes at about 210° with the formation of tripropyl phosphate and the salt PO_4Pr^aPb . *Barium monopropyl phosphate*, $PO_4Pr^aBa + 2H_2O$, is efflorescent; 100 parts of the aqueous solution contain 8·08 of the anhydrous salt at 20·5°, 6·98 at 60°, and 3·87 at 85°.

Triisopropyl phosphate, $PO_4Pr^b_3$, is a colourless liquid of agreeable odour, which boils at 136° under 68 mm. pressure, and is insoluble in water. *Barium monoisopropyl phosphate*, $PO_4Pr^bBa + 2H_2O$, crystallises

in nacreous scales; the weight of the anhydrous salt contained in 100 parts of the aqueous solution is 3.52 at 16°, 3.16 at 50°, and 1.7 at 85°.

Triisobutyl phosphate could only be obtained in an impure state, since it decomposes on distillation, even under diminished pressure. *Lead diisobutyl phosphate* forms small crystals melting at 169–170°, and is very soluble in water. *Barium monoisobutyl phosphate* crystallises with 2H₂O and is efflorescent; 100 parts of the aqueous solution contain 5.65 of the anhydrous salt at 24°, 3.30 at 52°, and 2.57 at 85°.

The solubility in water of the trialkyl phosphates decreases with increasing molecular weight, the methyl and ethyl esters being miscible with water in all proportions, whilst the butyl salt is insoluble. The lead salts, (PO₄R₂)₂Pb, where R is methyl, ethyl, propyl, *isopropyl*, or *isobutyl*, are more soluble in hot than in cold water, but the solubility of the barium salts of the composition PO₄RBa decreases as the temperature rises, except in the case of the ethyl compound, which possesses a maximum solubility at 40°. The amyl derivatives are different in character, the lead and barium salts being almost insoluble in water.

N. L.

Mixed Anhydrides of Formic Acid. By AUGUSTE BÉHAL (*Ann. Chim. Phys.*, 1900, [vii], 20, 411–432).—Most of the facts dealt with in this paper have already appeared (Abstr., 1899, i, 734), but the following are new.

sec-Octyl formate, obtained by the interaction of *sec*-octyl alcohol and formic acetic anhydride, boils at 186–187° under the ordinary pressure, and has a sp. gr. 0.8852 at 0°; its odour resembles that of cucumber.

Allyl formate boils at 87°, not at 82–83° as stated by Tollens (*Zeit. Chem.*, 1866, 2, 18; 1868, 4, 41).

The product obtained by acting on linalool with formic acetic anhydride boils at 125–127° under 30 mm. pressure, and has a sp. gr. 0.9672 at 0°; it consists probably of a mixture of *linalyl* and *geraniyl formates*, since on hydrolysis it yields linalool and geraniol.

Benzyl formate boils at 202–203° under 747 mm. pressure, and has a sp. gr. 1.081 at 23°.

d-Bornyl formate (Bertram and Walbaum, Abstr., 1893, i, 659, and 1894, i, 204) boils at 106–108° under 21 mm. pressure, and has a sp. gr. 1.027 at 0°, and 1.009 at 22°; [α]_D + 48°45'. *l*-Bornyl formate boils at 106–108° under 21 mm. pressure, has a sp. gr. 1.026 at 0°, and 1.009 at 22°, and [α]_D – 48°56' (compare Tschugaeff, Abstr., 1898, ii, 495).

Terpinyl formate, obtained from terpinol melting at 35°, boils at 127–128° under 30 mm., and has a sp. gr. 0.9945 at 0° (compare Lafont, Abstr., 1888, 495).

Menthyl formate boils at 219° under the ordinary pressure, and has a sp. gr. 0.9499 at 0°, and 0.9396 at 15°; [α]_D – 80.17.

Cinnamyl formate boils at 138–139° under 23 mm. pressure, and has a sp. gr. 1.086 at 0°.

Caryophyllenyl formate boils at 165–167° under 20 mm. pressure, and has a sp. gr. 1.0266 at 0°.

Santalyl formate boils at 175—178° under 27 mm. pressure, and has a sp. gr. 1·0180 at 0°.

The monoformic and diformic esters of glycols can usually be purified only with difficulty. *Glycol diformate*, $C_4H_6O_4$, boils at 88—89° under 25 mm. pressure, and has a sp. gr. 1·193 at 0°. *Pinacone monoformate*, $C_7H_{14}O_3$, boils at 90° under 20 mm. pressure. *Styrolene diformate*, $C_{10}H_{10}O_4$, boils at 164—165° under 25 mm. pressure, and has a sp. gr. 1·2091 at 0°. *Terpin diformate*, $C_{12}H_{20}O_4$, is a viscous liquid with an orange-like odour; it boils at 176—177° under 40 mm. pressure, and has a sp. gr. 1·067 at 27°.

Monoformin, diformin, or triformin could not be obtained by combining glycerol with formic acetic anhydride, owing to the acetyl radicle of the mixed anhydride entering into action to yield *glyceryl acetodiformate*, $C_7H_{10}O_6$; this boils at 157° under 27 mm. pressure, and has a sp. gr. 1·249 at 0°.

Formic acetic anhydride does not act on phenols in the cold, but on warming, acetates, and not formates, are obtained. With ammonia or primary or secondary amines, the corresponding formamides are produced. Methylformanilide, $NMePh \cdot CHO$, melts at 8°, boils at 142° under 20 mm. pressure, and has a sp. gr. 1·107 at 0°. *o-Formaminophenol*, $CHO \cdot NH \cdot C_6H_4 \cdot OH$, crystallises from water or from a mixture of benzene and alcohol, and melts at 125°. *p-Ethoxyformanilide*, $OEt \cdot C_6H_4 \cdot NH \cdot CHO$, crystallises from water and melts at 68·5°. *o-Phenylenediamine* does not give rise to a formamide, but yields phenylmethenylamidine, $C_6H_4 \cdot \begin{smallmatrix} N \\ \diagup \quad \diagdown \\ NH \end{smallmatrix} CH$ (Wundt, Abstr., 1878, 667).

Formic acid interacts with propionic, butyric, and *isovaleric* anhydrides, apparently yielding mixed anhydrides analogous to formic acetic anhydride; like the latter, they are decomposed by tertiary bases, yielding carbon monoxide; *sec*-octyl alcohol in all cases gives rise to *sec*-octyl formate.

Incidentally, a method of estimating formic acid by means of iodic acid is described, based on the reaction $2HIO_3 + 5HCO_2H = 5CO_2 + 6H_2O + I_2$; a weighed quantity of the substance containing formic acid is boiled for 1 hour in a reflux apparatus with 20 c.c. of a 50 per cent. solution of iodic acid, the iodine thus liberated distilled into aqueous potassium iodide, and titrated against sodium thiosulphate.

W. A. D.

Reduction of Oleic to Stearic Acid by the Aid of Nascent Hydrogen. By J. FREUNDLICH and OTTO ROSAUER (*Chem. Zeit.*, 1900, 24, 566).—The authors have tried Tissier's method for the reduction of oleic acid by the aid of water and granulated zinc under pressure; they find that the amount of stearic acid formed is small (1·7—3·79 per cent.), but that considerable quantities of zinc soaps are produced.

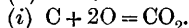
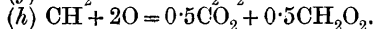
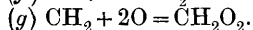
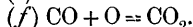
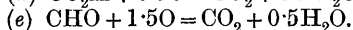
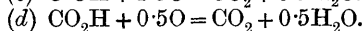
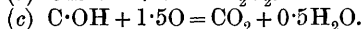
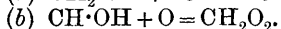
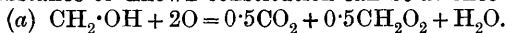
J. J. S.

Campholytic and isoLauronolic Acids. By G. BLANC (*Bull. Soc. Chim.*, 1900, [iii], 23, 695—701).—When the nitrile, $C_8H_{13}CN$, which Forster (*Trans.*, 1899, 75, 1141) obtained from camphoroxime, is reduced with sodium and boiling alcohol, it is converted into

α -aminocampholene, which was identified by means of its ureide and oxamide. The greater part of the paper is devoted to a discussion of the bearing of this result and of the researches of Forster (*loc. cit.*) and Walker (Trans., 1893, 63, 495; 1895, 67, 347; 1900, 77, 374) on the constitution of campholytic and isolauronic acids. N. L.

Glycollic and Glyoxylic Acids. By CARL BOETTINGER (*Chem. Zeit.*, 1900, 24, 619—620).—Glycolloglycollic acid, together with a small amount of glycolide, is formed when glycollic acid is boiled for 2 hours with acetic anhydride or when the acid is treated with boric and acetic anhydrides; when rapidly distilled, it passes over unaltered, otherwise it rapidly chars. The acid is readily hydrolysed to glycollic acid, and its calcium salt has the composition $(C_4H_5O_5)_2Ca, 2H_2O$. No well-defined products have been obtained by the action of acetic anhydride on glyoxylic acid. The following salts of glyoxylic acid have been prepared, C_2HO_3K, H_2O and $(C_2HO_3)_2Ba, 4H_2O$. J. J. S.

Oxidation of Dibasic Acids of the Aliphatic Series by Acid Potassium Permanganate. By LÉON PERDRIX (*Bull. Soc. Chim.*, 1900, [iii], 23, 645—660).—It has been previously shown (Abstr., 1897, i, 177) that the majority of polyhydric alcohols and their derivatives are oxidised by acidified potassium permanganate solution at the boiling temperature to carbon dioxide, formic acid, and water, the relative proportion of these products depending on the constitution of the substance oxidised. In the present paper, the behaviour of a number of acids is studied, and the following extended table representing the modes of oxidation of the different atomic groups is given. From these data, the equation representing the oxidation of a substance of known constitution can be at once deduced.



These results are shown to hold for mesoxalic, acetonedicarboxylic, itaconic, citric, fumaric, and maleic acids. Adipic, pimelic, and suberic acids resemble succinic acid in being scarcely, if at all, attacked by acidified potassium permanganate. Alkyl groups in side chains are not destroyed on oxidation, and when connected with a CH group the equation $\text{R} \cdot \text{CH} \cdot + 2\text{O} = \text{R} \cdot \text{CO}_2\text{H}$ is found to hold. Thus, isosuccinic acid yields acetic acid, and ethylmalonic acid yields propionic acid. Lactide and pyrotartaric, citraconic, and mesaconic acids are other examples of this class. N. L.

Substitution Products of Tetronic Acid. By LUDWIG WOLFF (*Annalen*, 1900, 312, 119—132. Compare Abstr., 1896, i, 522).—An introduction to the following papers. M. O. F.

Nitrotetronic Acid, Aminotetronic Acid, and their Derivatives. By LUDWIG WOLFF and A. LÜTTRINGHAUS (*Annalen*, 1900,

312, 133—155).—*Nitrotetronic acid*, $\text{OH}\cdot\text{NO}\cdot\overset{\text{CO}\cdot\text{CH}_2}{\underset{\text{CO}}{\text{C}}}\text{>O}$, prepared by the action of fuming nitric acid on tetronic acid, and also by oxidising oximinotetronic acid (Abstr., 1896, i, 524) with nitric or chromic acid, crystallises from hot water in lustrous prisms containing $2\text{H}_2\text{O}$, and melts, evolving gas, at 184° ; the *barium* salt separates from hot water in triclinic crystals containing $4\text{H}_2\text{O}$, and the *silver* salt contains $1\text{H}_2\text{O}$. The *hydroxylamine* salt forms nacreous leaflets and melts at 194 — 195° , evolving gas; the *methyl* ether crystallises from alcohol or water in small, yellowish, six-sided plates, and melts at 143 — 144° , evolving gas. The *phenylhydrazone*, $\text{OH}\cdot\text{NO}\cdot\overset{\text{NHPH}\cdot\text{N}\cdot\text{C}\cdot\text{CH}_2}{\underset{\text{CO}}{\text{C}}}\text{>O}$,

is sparingly soluble in common media, crystallises from glacial acetic acid in small, yellowish-brown prisms, and melts at 184 — 186° , when it decomposes. The *oxime*, $\text{NOH}\cdot\overset{\text{C}\cdot\text{CH}_2}{\underset{\text{CO}}{\text{C}}}\text{>O}$, crystallising from hot water in white, lustrous plates or prisms containing $1\text{H}_2\text{O}$, becomes yellow at 140° , and melts, evolving gas, at 147° ; the *silver* salt is crystalline, and the *barium* salt forms aggregates of pale yellow needles, whilst the *methyl* ether separates from methyl alcohol in pale yellow, six-sided plates melting and decomposing at 154 — 155° .

Aminotetronic acid, $\text{OH}\cdot\overset{\text{C}\cdot\text{CH}_2}{\underset{\text{CO}}{\text{C}}}\text{>O}$, prepared by reducing nitrotetronic acid with sodium amalgam, or, in acid solution, with zinc or tin, crystallises from dilute alcohol in colourless needles, which become yellow at 150° and char above 250° ; it is very readily soluble in water, the solution, which is acid, decomposing carbonates, and developing a pale red coloration with ferric chloride. The *dibenzoyl* derivative crystallises from alcohol or benzene in slender needles melting at 164° , and is readily hydrolysed to the *benzoyl* derivative,

$\text{OH}\cdot\overset{\text{C}\cdot\text{CH}_2}{\underset{\text{CO}}{\text{C}}}\text{>O}$, which crystallises in long needles or four-sided prisms, and melts at 178° ; boiling aniline converts the latter substance into the *anilide* of benzylaminotetronic acid, which crystallises from alcohol in colourless prisms and melts at 191 — 192° .

The *anhydride* of diazotetronic acid, $\text{N}\leq\overset{\text{O}\cdot\text{C}\cdot\text{CH}_2}{\underset{\text{CO}}{\text{N}\cdot\text{C}}}\text{>O}$, produced when aminotetronic acid is treated with nitrous acid, crystallises from a mixture of chloroform and petroleum in lustrous, four-sided plates, and melts at 93° ; aqueous or acid solutions are stable towards iodine, hydroxylamine hydrochloride, sulphurous acid, or oxidising agents, but alkalis, and solutions of alkali salts such as sodium acetate, nitrite, or cyanide, decompose it rapidly. The aqueous solution develops a colouring matter with the sodium derivative of α -naphthol. *Glycolglycollic acid*, $\text{OH}\cdot\text{CH}_2\cdot\text{CO}\cdot\text{O}\cdot\text{CH}_2\cdot\text{CO}_2\text{H}$, results from hydrolysing diazotetronic anhydride with barium hydroxide, and crystallises from ether in colourless prisms or six-sided plates melting at 99 — 100° ; the *calcium* salt contains $4\frac{1}{2}\text{H}_2\text{O}$.

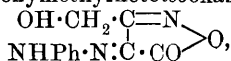
Sodium diazotetronoculjhona e, $\text{ONa} \cdot \text{C} \cdot \text{CH}_2 \text{O} \text{SO}_3\text{Na} \cdot \text{N} \cdot \text{N} \cdot \text{C} \cdot \text{CO}$, prepared by treating diazotetronic anhydride with sodium sulphite, crystallises from water in small, pale yellow needles containing $3\text{H}_2\text{O}$; the aqueous solution is neutral, and reduces ammoniacal silver nitrate, mercuric chloride, and Fehling's solution. The *hydrogen potassium salt*, $\text{C}_4\text{H}_5\text{O}_3\text{N}_2 \cdot \text{SO}_3\text{K}$, is much less readily soluble than the sodium salt, and crystallises from water in aggregates of lustrous yellow needles or leaflets.

The *anhydride* of dihydrodiazotetronic acid, $\text{NH} \langle \text{O} \cdot \text{C} \cdot \text{CH}_2 \rangle \text{O}$, formed on adding the finely powdered sodium salt of diazotetronosulphonic acid to concentrated hydrochloric acid, crystallises from water or alcohol in yellowish leaflets melting and decomposing at 190° ; it is readily oxidised to the anhydride of diazotetronic acid, merely boiling an alcoholic solution sufficing to effect this change. Aqueous hydroxylamine hydrochloride converts the anhydride into the compound $\text{C}_4\text{H}_5\text{O}_3\text{N}_3$, which may be represented by one of the formulæ, $\text{NH} \langle \text{C} \cdot \text{CH}_2 \rangle \text{O}$ and $\text{NH} \langle \text{N}(\text{OH}) \cdot \text{C} \cdot \text{CH}_2 \rangle \text{O}$; it crystallises from much boiling water in small, yellowish needles, which become brown about 220° , and undergo profound decomposition at about 250° . When suspended in water, the oxime quickly reduces mercuric chloride, losing nitrogen and becoming converted into *β-oximinobutyrolactone*, $\text{NOH} \cdot \text{C} \cdot \text{CH}_2 \text{CO}$, which crystallises from hot water in colourless, four-sided plates, and decomposes at 146° ; nitrous acid converts it into dioximinobutyrolactone (compare *loc. cit.*).
M. O. F.

Phenylhydrazone of Diketobutyrolactone. By LUDWIG WOLFF and A. LÜTTINGHAUS (*Annalen*, 1900, 312, 155—162).—The *phenylhydrazone* of diketobutyrolactone, $\text{NHPh} \cdot \text{N} \cdot \text{C} \cdot \text{CH}_2 \text{CO}$, prepared by adding freshly diazotised aniline to an aqueous solution of potassium tetronate, crystallises from glacial acetic acid in small, golden yellow needles, and melts, evolving gas, at 210° ; it reduces Fehling's solution, and develops a deep blue coloration with concentrated sulphuric acid and potassium dichromate. The phenylhydrazone dissolves in ammonia, or sodium hydroxide or carbonate, forming yellow salts of an unstable, monobasic, benzeneazotetronic acid; the *calcium salt* forms yellow needles, and the *silver salt* is also crystalline. The *benzoyl derivative* crystallises from a mixture of chloroform and petroleum in brick-red prisms, and melts at 142° .

The *osazone* of diketobutyrolactone, $\text{NHPh} \cdot \text{N} \cdot \text{C} \cdot \text{CH}_2 \text{CO}$, produced by the action of phenylhydrazine on the phenylhydrazone, crystallises from boiling acetic acid in red plates which decompose at 242° , and in orange-yellow needles which become red at 180° , and melt also at 242° , when they decompose; it is insoluble in sodium carbonate, but yields a yellowish-red solution in hot sodium hydroxide.

The *phenylhydrazoxime* of diketobutyrolactone, $\text{NOH}:\text{C}:\text{CH}_2\text{>O}$,
 $\text{NHPH}\cdot\text{N}:\text{C}-\text{CO}$, obtained by the action of hydroxylamine hydrochloride on the phenylhydrazone, crystallises from boiling alcohol in yellowish-green needles, melting and decomposing at 236° . Hydrolysis resolves this compound into the *acid*, $\text{NOH}:\text{C}(\text{CH}_2\cdot\text{OH})\cdot\text{C}(\text{CO}_2\text{H})\cdot\text{N}\cdot\text{NHPH}$, which crystallises from dilute alcohol in lustrous yellow needles decomposing at $147-148^\circ$. When the alcoholic solution of the acid is boiled with dilute hydrochloric acid, the phenylhydrazoxime is regenerated, but the action of boiling 30 per cent. acetic acid converts it into the *phenylhydrazone* of hydroxymethylketoisooxazolone,



which crystallises from boiling alcohol in lustrous, golden-yellow needles melting and decomposing at 165° ; the *silver* salt is very sparingly soluble in water. M. O. F.

Behaviour of α -Methyltetronic Acid towards Diazobenzene Chloride. By LUDWIG WOLFF and WILLY HEROLD (*Annalen*, 1900, 312, 163—164).—The *phenylhydrazone* of pyruvoglycollic acid, $\text{CO}_2\text{H}\cdot\text{CH}_2\cdot\text{O}\cdot\text{CO}\cdot\text{CMe}:\text{N}\cdot\text{NHPH}$, prepared by adding diazobenzene chloride to α -methyltetronic acid, crystallises from hot water in pale yellow needles containing $2\text{H}_2\text{O}$; the anhydrous acid melts at $163-164^\circ$, and the solution in concentrated sulphuric acid develops a deep red coloration with potassium dichromate.

Boiling water resolves the substance into glycollic acid and the phenylhydrazone of pyruvic acid. M. O. F.

Iodotetronic Acid and Sulphotetronic Acid. By LUDWIG WOLFF and EDUARD FERTIG (*Annalen*, 1900, 312, 164—170).—*Iodo-*

tetronic acid, $\text{OH}\cdot\text{C}:\text{CH}_2\text{>O}$,
 $\text{Cl}\cdot\text{CO}$, prepared by the action of iodine on tetronic acid in presence of iodic acid, crystallises from hot water in small, white needles, which become coloured on exposure to light, and melts and decomposes at $178-180^\circ$; it is strongly acidic, and develops a violet-red coloration with ferric chloride. Sodium nitrite solution dissolves iodotetronic acid, developing a violet coloration, and producing sodium oximinotetronate; potassium iodide liberates iodine, regenerating tetronic acid. The *silver* salt crystallises from boiling water in small, white needles which are sensitive to light.

Dichlorotetronic acid, $\text{CO}\cdot\text{CH}_2\text{>O}$,
 $\text{CCl}_2\cdot\text{CO}$, produced when chlorine is passed into chloroform holding iodotetronic acid in suspension, crystallises from petroleum in small needles and melts at $55-57^\circ$; ammonia gives rise to dichloroacetamide.

Chlorobromotetronic acid, $\text{CO}-\text{CH}_2\text{>O}$,
 $\text{CClBr}\cdot\text{CO}$, obtained by the action of chlorine on bromotetronic acid suspended in chloroform, crystallises from a mixture of ether and petroleum in small, colourless needles melting at $73-74^\circ$. Concentrated ammonia gives rise to chlorobromoacetamide, which melts at $125-126^\circ$.

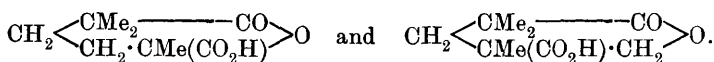
Tetronosulphonic acid, $\text{OH} \cdot \text{C} \cdot \text{CH}_2 \begin{array}{c} | \\ \text{SO}_3\text{H} \cdot \text{C} - \text{CO} \end{array} \text{O}$, prepared by dissolving tetric acid in 3 parts of fuming sulphuric acid, crystallises from a mixture of ether and alcohol in flat needles melting at 83° ; it is hygroscopic, and develops a deep red coloration with ferric chloride. The *lead* salt forms needles containing $2\text{H}_2\text{O}$, and the *barium* salt contains $4\text{H}_2\text{O}$.
M. O. F.

Action of Aluminium Chloride on Camphoric Anhydride. By G. BLANC (*Bull. Soc. Chim.*, 1900, [iii], 23, 693—695).—Observations on the claim to priority put forward by Perkin (*Proc.*, 1900, 16, 18), whose results are considered to furnish fresh proofs of the correctness of the formula assigned by the author to *isolauronic* acid.
N. L.

Action of Zinc on a Mixture of Ethyl Bromoisobutyrate and Ethyl Formate. II. Action of Hydriodic, Hydrobromic, and Sulphuric Acids on β -Hydroxy-*s*-tetramethylglutaric Acid. By JAKOV I. MICHAILENKO and W. P. JAVORSKY (*J. Russ. Phys. Chem. Soc.*, 1900, 32, 328—346. Compare Abstr., 1899, i, 482).—When β -hydroxy-*s*-tetramethylglutaric acid is heated in sealed tubes with concentrated hydriodic acid at 130 — 135° , it is reduced, yielding a mixture of lactonic acids in addition to the expected *s*-tetramethylglutaric acid, $\text{CH}_2(\text{CMe}_2 \cdot \text{CO}_2\text{H})_2$, which crystallises from hot water in long needles melting at 185 — 186° ; the *potassium* (with $2\text{H}_2\text{O}$), *barium* (with $3\text{H}_2\text{O}$), *lead* (with $2\text{H}_2\text{O}$), *silver*, *potassium hydrogen*, and *barium hydrogen* (with $4\text{H}_2\text{O}$) salts were prepared. By the action of acetyl chloride on the acid, the corresponding *anhydride*, $\text{CH}_2 \begin{array}{c} \text{CMe}_2 \cdot \text{CO} \\ \text{CMe}_2 \cdot \text{CO} \end{array} \text{O}$, is formed; it separates from ether in long, slender needles melting at 86 — 87° , and with *p*-toluidine in molecular proportion gives the corresponding *amino-acid*, $\text{C}_{11}\text{H}_{23}\text{O}_3\text{N}$, which crystallises from benzene in transparent, yellowish plates melting at 157 — 158° , slightly soluble in water and readily so in alcohol.

The mixture of lactonic acids also formed during the reduction of the hydroxy-acid with hydriodic acid has a melting point of 116 — 120° , and after long-continued fractional crystallisation is separated into two monobasic *acids*, both having the composition $\text{C}_9\text{H}_{14}\text{O}_4$. The first of these, melting at 141 — 142° , forms transparent crystals, and gives a *potassium* salt crystallising from alcohol in transparent plates; the other, which could not be obtained pure, melts at about 116° ; their *barium* salts separate in anhydrous plates. Barium hydrogen salts could not be obtained, and acetyl chloride is without action on the acids. The action of concentrated or dilute sulphuric acid or of hydrobromic acid on β -hydroxy-*s*-tetramethylglutaric acid also yields the same two lactonic acids, but in the case of hydrobromic acid a purer product is formed, the second acid being obtained in opaque aggregates of long crystals melting at 120 — 124° . That these acids are saturated monobasic acids is shown by their affinity constants, which have the values K 0.00128 (acid melting at 141 — 142°) and 0.00150 (acid melting at 120 — 124°). On heating these lactonic acids

with potassium hydroxide or barium hydroxide, a dibasic acid is obtained isomeric with the original hydroxy-acid, as is shown by its *barium* salt, which forms fibrous crystals, insoluble in alcohol, and has the composition $C_9H_{14}O_5Ba, 3H_2O$; the free acid could not be prepared, as on decomposing the salts with acid, the lactonic acids are reformed. The two lactonic acids have probably the constitutions:



On oxidising β -hydroxy-*s*-tetramethylglutaric acid with nitrogen oxides, dimethylmalonic and *isobutyric* acids are first formed, the latter being then decomposed with the formation of acetic acid.

T. H. P.

Researches in the Pyrone Group. VIII. Diethyl Comenate. By RICCARDO OLIVERI-TORTORICI (*Gazzetta*, 1900, 30, ii, 16—23).—*Diethyl comenate*, $OEt \cdot C_5H_2O_2 \cdot CO_2Et$, obtained by the action of ethyl iodide on the silver derivative of the monoethyl salt, forms acicular, colourless crystals ($+ H_2O$), melts at $79-80^\circ$, and dissolves in water, alcohol, ether, chloroform, or benzene. When boiled for 3—4 hours with water, it is wholly converted into ethylcomenic acid, which, when hydrolysed by barium hydroxide, yields molecular proportions of acetylcarbiny ethyl ether and oxalic and formic acids. T. H. P.

[**Tartrates of Nickel and Cobalt.**] By OLIN F. TOWER (*J. Amer. Chem. Soc.*, 1900, 22, 501—521).—Nickel tartrate was first obtained by Werther (*J. pr. Chem.*, 1844, 32, 400) by saturating a boiling solution of tartaric acid with freshly precipitated nickel hydroxide; his observations are confirmed, except that whilst he considered the salt to be crystalline, the present author regards it as amorphous. Nickel tartrate may also be prepared by the action of tartaric acid on the carbonate. Cobalt tartrate may be similarly obtained by either method; it is precipitated as a pale pink powder, and closely resembles nickel tartrate in its general properties. The potassium nickel tartrate obtained by Fabian (*Annalen*, 1857, 103, 248) by the action of potassium hydrogen tartrate on nickel carbonate was also prepared, but an attempt to produce the corresponding cobalt salt resulted only in the formation of a mixture of the tartrates of cobalt and potassium.

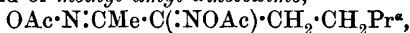
A series of determinations of the depression of the freezing point and of the conductivity of solutions of these nickel and cobalt tartrates yielded results which seem to point to the existence of a polymerised chemical structure.

When potassium hydroxide and nickel tartrate are mixed in molecular proportion, a gelatinous mass is formed which appears to be a hydrated form of potassium nickel tartrate; cobalt tartrate, under the same conditions, yields a flocculent precipitate of variable composition; in each case, the product is soluble in excess of potassium hydroxide. The author concludes from the results of his experiments that these precipitates dissolve in excess of the reagent on account of the formation of a compound in which the nickel or cobalt replaces the hydrogen atoms of the alcoholic hydroxyl groups of tartaric acid. E. G.

Conversion of Ketones into α -Diketones. V. *iso*Propyl *iso*-Butyl Ketone. By GIACOMO PONZIO (*Gazzetta*, 1900, 30, ii, 23—27).—*iso*Propyl *isobutyl ketone*, $\text{CHMe}_2 \cdot \text{CO} \cdot \text{CH}_2 \cdot \text{CHMe}_2$, prepared by the action of zinc *isobutyl* on *isobutyryl* chloride, is a mobile liquid boiling at 147—148° under 744 mm. pressure, and having an agreeable odour resembling that of camphor. The *oxime*, $\text{C}_8\text{H}_{17}\text{ON}$, boils unchanged at 201—203°. On oxidation with nitric acid, the ketone yields diisopropyl diketone and dinitroisobutane, $\text{CHMe}_2 \cdot \text{CH}(\text{NO}_2)_2$ (compare Abstr., 1897, i, 317; 1899, i, 111). The *potassium* derivative of dinitroisobutane, $\text{CHMe}_2 \cdot \text{CK}(\text{NO}_2)_2$, crystallises from alcohol in sparkling yellow laminae. T. H. P.

Acetyldioximes of α -Diketones. By GIACOMO PONZIO (*Gazzetta*, 1900, 30, ii, 27—30).—The melting point cannot be used as a means of characterising the dioximes of α -diketones, since these compounds generally melt at about 170°. For this purpose, the best derivatives to use are the diacetyl compounds of the dioximes, which are readily prepared by heating the dioximes with a slight excess of acetic anhydride.

The *diacetyl* derivative of *dimethyl diketoxime*, $\text{C}_2\text{Me}_2(\text{NOAc})_2$, separates from alcohol in shining needles which melt at 112° and dissolve in ether, light petroleum, or benzene. The *diacetyl* derivative of *methyl ethyl diketoxime*, $\text{OAc} \cdot \text{N} \cdot \text{CMe} \cdot \text{CET} \cdot \text{N} \cdot \text{OAc}$, crystallises from aqueous alcohol in sparkling prisms which melt at 68—69°, and are soluble in alcohol, benzene, or light petroleum. The *diacetyl* derivative of *methyl propyl diketoxime*, $\text{OAc} \cdot \text{N} \cdot \text{CMe} \cdot \text{CPr} \cdot \text{N} \cdot \text{OAc}$, is a dense, colourless liquid decomposing on boiling at the ordinary pressure, that of *methyl isobutyl diketoxime*, $\text{OAc} \cdot \text{N} \cdot \text{CMe} \cdot \text{C}(\text{N} \cdot \text{OAc}) \cdot \text{CH}_2 \cdot \text{CHMe}_2$, separates from light petroleum in shining prisms melting at 42°, whilst the *diacetyl* compound of *methyl amyl diketoxime*,



is a dense oil. The *dibenzyl* derivative of *methyl ethyl diketoxime*, $\text{CH}_2\text{Ph} \cdot \text{O} \cdot \text{N} \cdot \text{CMe} \cdot \text{CET} \cdot \text{N} \cdot \text{O} \cdot \text{CH}_2\text{Ph}$, crystallises from alcohol in white plates melting at 62—63°. T. H. P.

Derivatives of Dextrose. By WILHELM KOENIGS and EDUARD KNORR (*Chem. Centr.*, 1900, ii, 179—180; from *Sitzungsber. Bayr. Akad. Wiss.*, 1900, 103—105).—*Bromotetracetoxydextrose*, $\text{C}_6\text{H}_7\text{BrO}(\text{OAc})_4$, prepared by the action of acetyl bromide on grape sugar, melts at 88—89°, is soluble in light petroleum or ether, but scarcely so in water; it is dextrorotatory and reduces boiling Fehling's solution. By allowing a solution of bromotetracetoxydextrose in methyl alcohol to remain for some time, β -methylglucoside is formed, and by the action of dry silver carbonate or nitrate, tetracetyl- β -methylglucoside is obtained. A solution in ethyl alcohol similarly yields corresponding ethyl derivatives. Tetracetylmethylglucoside and tetracetylethylglucoside melt at 104—105° and at 105—106° respectively; both are laevorotatory, do not reduce Fehling's solution, and are slowly hydrolysed by a cold solution of sodium hydroxide. Pentacetyldextrose, melting at 130—131°, is formed by shaking silver acetate with a solution of bromotetracetoxydextrose in glacial acetic acid. E. W. W.

Nitrocelluloses. By LÉO VIGNON (*Compt. rend.*, 1900, 131, 509—511).—The nitrocelluloses and nitro-oxycelluloses energetically reduce Pasteur's cupropotassium solution, the reducing power in all cases being independent of the degree of nitration, and equal to about one-fifth that of invert sugar. Since, moreover, it is sensibly the same for both nitrated cellulose and for nitrated oxycellulose, and since cellulose and hydrocellulose are destitute of reducing power, although oxycellulose is strongly reducing (*Abstr.*, 1898, i, 619), it follows that the product of either the partial or complete nitration of cellulose is not a nitrocellulose, but a nitro-oxycellulose. W. A. D.

Dextrins of Saccharification. By PAUL PETIT (*Compt. rend.*, 1900, 131, 453—455. Compare *Abstr.*, 1899, i, 559).—The author has investigated the action of diastase on starch paste at 50°, 60°, and 70°, and also on the products of this reaction. The results vary greatly with the age of the diastase and the manner in which it has been kept, and hence the processes have no industrial value.

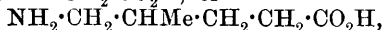
C. H. B.

Action of Hexamethylenetetramine on the Esters of Chloroacetic and Bromoacetic Acids. By R. LOCQUIN (*Bull. Soc. Chim.*, 1900, [iii], 23, 660—663).—Hexamethylenetetramine reacts with methyl chloroacetate in chloroform solution to form a *compound*, $C_6H_{12}N_4 \cdot CH_2Cl \cdot CO_2Me$, which forms large, colourless crystals melting at 141°. With ethyl bromoacetate, a similar *compound*, $C_6H_{12}N_4 \cdot CH_2Br \cdot CO_2Et$, melting at 172—173°, is obtained. When heated with alcoholic hydrobromic acid, this is decomposed with the formation of *ethyl aminoacetate hydrobromide*; this substance, now prepared for the first time, crystallises in long, colourless needles melting at 166°.

N. L.

Terpenes and Etheral Oils: Ring Disruption among Cyclic Ketones. By OTTO WALLACH (*Annalen*, 1900, 312, 171—210. Compare this vol., i, 44).—The study of oximes derived from the simplest saturated ketones shows that conversion into an isomeride depends on the transference of nitrogen, in the form of an imino-group, to a position between two carbon atoms of the ring, producing a lactam; the lactam obtained in this way is readily hydrolysed to the corresponding amino-acid, the process affording a convenient means for preparing members of this class. *cyclo-Pentanoneoxime*, for instance, when gently heated with sulphuric acid containing 16 per cent. of water, is converted into 2-piperidone, $CH_2 \begin{smallmatrix} \text{CH}_2 - \text{CO} \\ \text{CH}_2 \cdot \text{CH}_2 \end{smallmatrix} \text{NH}$, which yields δ -aminovaleric acid, $NH_2 \cdot CH_2[CH_2]_2 \cdot CH_2 \cdot CO_2H$, on hydrolysis.

Sulphuric acid (10 parts: 2 parts of water) converts β -methylcyclopentanoneoxime (melting at 86°) into the *isooxime*, $C_6H_{11}ON$, which crystallises in long needles, melts at 87°, and boils at 147—148° under 15 mm. pressure; it has $[\alpha]_D + 75^\circ$ in water, and forms a white *hydrochloride* which melts at 148—149°. *Aminocaproic acid*, $NH_2 \cdot CH_2 \cdot CH_2 \cdot CHMe \cdot CH_2 \cdot CO_2H$, or



prepared by heating the hydrochloride of the *iso-oxime* with 20 per

cent. hydrochloric acid at 150° , melts at $133\text{--}135^{\circ}$, and is extremely soluble in water.

cyclo-Hexanoneoxime, $\text{CH}_2 \begin{smallmatrix} \text{CH}_2 \cdot \text{CH}_2 \\ \text{CH}_2 \cdot \text{CH}_2 \end{smallmatrix} \text{C} \cdot \text{NOH}$, is readily converted into the *iso*-oxime, $\begin{smallmatrix} \text{CH}_2 \cdot \text{CH}_2 \cdot \text{CH}_2 \\ \text{CH}_2 - \text{CH}_2 - \text{CO} \end{smallmatrix} \text{NH}$, which separates from ether in well-formed crystals melting at $68\text{--}70^{\circ}$ and boils at 139° under 12 mm. pressure; the *hydrochloride* is deliquescent, and melts at $73\text{--}75^{\circ}$. ϵ -Aminocaproic acid (ϵ -*leucine*), $\text{NH}_2 \cdot \text{CH}_2 \cdot [\text{CH}_2]_3 \cdot \text{CH}_2 \cdot \text{CO}_2\text{H}$, prepared by heating the *iso*-oxime with hydrochloric acid, crystallises from aqueous solutions to which alcohol has been added, and melts, evolving gas, at $201\text{--}202^{\circ}$ (compare Gabriel and Maass, Abstr., 1899, i, 595).

$\delta\epsilon$ -Hexenic acid, $\text{CH}_2 \cdot \text{CH} \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{CO}_2\text{H}$, produced on treating the hydrochloride of ϵ -aminocaproic acid with sodium nitrite, melts at $208\text{--}210^{\circ}$, and has a sp. gr. 0.962; the refractive index n_D is 1.4345 at 23° , and the molecular refraction, 30.89. The *ammonium* salt is crystalline, and yields the *silver* salt with silver nitrate.

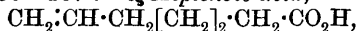
The *isooximes* of methyl*cyclohexanone* (this vol., i, 45) are separated with some difficulty, the α -modification, which melts at 105° and is more sparingly soluble in water than the isomeride, having $[\alpha]_D - 36.1^{\circ}$ in water; the β -*isooxime* melts at $68\text{--}69^{\circ}$, and has $[\alpha]_D - 22.2^{\circ}$ in water.

[With L. OTTEMANN.]—The *amino*-acid, $\text{C}_7\text{H}_{15}\text{O}_2\text{N}$, prepared from the α -*iso*-oxime, dissolves very readily in water, and melts, evolving gas, at $187\text{--}188^{\circ}$; the *amino*-acid from the β -*isooxime* melts at $145\text{--}147^{\circ}$. Both yield the unsaturated *acid*, $\text{C}_7\text{H}_{12}\text{O}_2$, which boils at $220\text{--}225^{\circ}$.

Aminodecenoic acid, $\text{C}_{10}\text{H}_{21}\text{O}_2\text{N}$, prepared from menthone*isooxime*, is scarcely soluble in alcohol and ether, but dissolves in water, from which it separates in well-formed crystals melting at $194\text{--}195^{\circ}$; the *benzoyl* derivative crystallises from methyl alcohol and melts at $127\text{--}128^{\circ}$, whilst the *ethyl* ester melts at $50\text{--}53^{\circ}$ and boils at $136\text{--}137^{\circ}$ under 12 mm. pressure. Nitrous acid converts it into *decenoic acid*, $\text{C}_{10}\text{H}_{18}\text{O}_2$, which boils at $257\text{--}259^{\circ}$ and is identical with menthonenic acid (Abstr., 1897, i, 428). It is probable that the aminodecenoic acid obtained from menthone*isooxime* has the constitution $\text{NH}_2 \cdot \text{CHPr}^e \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{CHMe}^e \cdot \text{CH}_2 \cdot \text{CO}_2\text{H}$.

Tetrahydrocarboxime also yields an *aminodecenoic acid*, $\text{C}_{10}\text{H}_{21}\text{O}_2\text{N}$, which separates from water in small, transparent crystals melting at $201\text{--}202^{\circ}$; nitrous acid converts it into the corresponding *decenoic acid*, $\text{C}_{10}\text{H}_{18}\text{O}_2$, which boils at $257\text{--}260^{\circ}$, has a sp. gr. 0.936, the refractive index n_D 1.4554 at 20° , and a molecular refraction 49.21.

Suberone*isooxime* has been described recently (*loc. cit.*); the *aurichloride* is well defined, and melts at $95\text{--}96.5^{\circ}$. Hydrolysis converts the *iso*-oxime into ζ -*amino*-*n*-heptoic (*aminocenanthoic*) *acid*, $\text{NH}_2 \cdot \text{CH}_2[\text{CH}_2]_4 \cdot \text{CH}_2 \cdot \text{CO}_2\text{H}$, which crystallises from water, and melts, evolving gas, at $186\text{--}187^{\circ}$. $\epsilon\zeta$ -*Heptenoic acid*,



obtained by the action of nitrous acid on aminoheptoic acid, boils at $225\text{--}227^{\circ}$, has a sp. gr. 0.952, the refractive index n_D 1.4425 at 17° ,

and a molecular refraction 35.61; the *ammonium* salt is crystalline, and yields the *silver* salt with silver nitrate. Oxidation with potassium permanganate gives rise to adipic acid, the aminoheptioic acid itself yielding pimelic acid.

M. O. F.

Behaviour and Reactions of Uric Acid and its Salts in Solution. By HIS, jun., and PAUL (*Chem. Centr.*, 1900, ii, 42; from *Berl. klin. Woch.*, 37, 420).—One part of uric acid dissolves in 88,000 parts of water; it decomposes even in pure aqueous solutions. Both the acid and its salts easily form supersaturated solutions. Colloidal solutions of the urates may also be obtained, and in this state there is no fixed limit to their solubility. From such solutions, the salt soon separates in a very finely divided form, and indeed the properties of the colloidal solutions resemble those of a liquid containing a finely divided solid in suspension rather than those of a true solution. The urates readily separate from solution in an amorphous form, and in this state their solubility is not the same as that of the crystallised salts. Attempts to prepare Rüdel's compound of uric acid and carbamide failed, the presence of carbamide neither affecting the solubility of uric acid nor preventing its precipitation by acids. Metallic salts such as those of potassium or lithium which form easily soluble urates cannot, however, affect the solubility of the acid sodium salt, for being dissociated into ions in solution, the least soluble salt is the first to separate or the last to dissolve. It is therefore impossible to render gouty accretions more soluble by means of potassium or lithium salts.

E. W. W.

Pentacyano-iron Compounds. By KARL A. HOFMANN (*Annalen*, 1900, 312, 1—33. Compare Abstr., 1896, i, 517, and Werner, Abstr., 1897, ii, 263).—In accordance with Werner's nomenclature of complex inorganic compounds, the author refers to sodium nitroprusside as *sodium nitrosopentacyanoferrate*, or, preferably, as *ferripentacyanonitrososodium*, $[\text{Fe}(\text{CN})_5\text{NO}]\text{Na}_2$. The substance obtained from it by the action of sodium hydroxide (Abstr., 1896, i, 269), then called quaternary sodium nitroprusside, $[\text{Fe}(\text{CN})_5\text{NO}_2]\text{Na}_4$, becomes *sodium nitropentacyanoferrite* or *ferropentacyanonitritosodium*. Oxidation with potassium permanganate converts this into the deep carmine-red compound, $[\text{Fe}(\text{CN})_5\text{NO}_2]\text{Na}_3$, called *sodium nitritopentacyanoferrite* or *ferropentacyanonitritosodium*.

Both sodium nitroprusside and the compound obtained from it by the action of sodium hydroxide readily part with the nitroso-group under the influence of phenylhydrazine, hydroxylamine, aldehyde, and acetone, the same effect being produced by oxidising agents such as potassium hypobromite, lead peroxide, or hydrogen peroxide; sodium prusside, $[\text{Fe}(\text{CN})_5\text{H}_2\text{O}]\text{Na}_3$, is thus produced, and is now called *sodium aquopentacyanoferrite* or *ferropentacyano-aquosodium*. Nitrous acid or bromine water oxidises this to the deep bluish-violet compound, $[\text{Fe}(\text{CN})_5\text{H}_2\text{O}]\text{Na}_2$, *sodium aquopentacyanoferrate* or *ferripentacyano-aquosodium*.

The foregoing five compounds yield *sodium amminopentacyanoferrite* or *ferropentacyano-ammoniosodium*, $[\text{Fe}(\text{CN})_5\text{NH}_3]\text{Na}_3$, when treated with ammonia; this was previously called sodium ammoniopruesside.

Oxidation with nitrous acid or bromine water converts it into *sodium amminopentacyanoferrate* or *ferripentacyano-ammoniosodium*, $[\text{Fe}(\text{CN})_5\text{NH}_3]\text{Na}_2$.

The two first named substances give rise to sodium arseniteprusside, $[\text{Fe}(\text{CN})_5\text{AsO}_2]\text{Na}_4$, under the influence of alkaline sodium arsenite; this is termed *sodium arsenitopentacyanoferrite* or *ferropentacyano-arsenitosodium*.

All the compounds mentioned yield sodium sulphiteprusside, $[\text{Fe}(\text{CN})_5\text{SO}_3]\text{Na}_5$, when treated with alkaline sodium sulphite (Abstr., 1896, i, 197); this is now called *sodium sulphitopentacyanoferrite*, or *ferropentacyanosulphitosodium*.

The groups or atoms associated with cyanogen in the foregoing nine substances may be replaced by cyanogen, forming sodium ferrocyanide, $[\text{Fe}(\text{CN})_6]\text{Na}_4$.

The compound, $[\text{Fe}(\text{CN})_5\text{NO}\cdot\text{SC}\cdot\text{NH}\cdot\text{NH}_2]\text{Na}_3$, is obtained by the action of thiocarbamide on sodium nitroprusside.

For experimental details relating to the preparation and identification of these compounds, reference must be made to the original paper.

M. O. F.

Isomerism in the Aromatic Series. By WILLIAM OECHSNER DE CONINCK (*Ann. Chim. Phys.*, 1900, [vii], 20, 136—144).—A theoretical paper in which the author cites evidence in favour of the view that two out of the three forms of a di-substitution derivative of benzene are closely related, and differ from the third; the data used include boiling and freezing points, heats of dissolution and formation, and chemical reactivity.

W. A. D.

Preparation of Iodoso- and Iodoxy-derivatives. By GIOVANNI ORTOLEVA (*Gazzetta*, 1900, 30, ii, 1—15).—A reply to the criticism of Willgerodt (this vol., i, 339) on the use of pyridine by the author (*Gior. Soc. Sci. Nat. Econ. Palermo*, 23, 1) for the preparation of iodoso- and iodoxy-compounds. A number of compounds have been prepared, the new results being as follows.

m-Iodosotoluene, $\text{C}_7\text{H}_7\text{OI}$, prepared by the action of water on a pyridine solution of *m*-tolyl iodochloride, forms a yellowish, amorphous mass decomposing and evolving gas at 180—185°; it is soluble in glacial acetic acid from which the *acetate* is deposited in white needles melting and decomposing at 147—149°.

m-Iodoxytoluene is obtained by oxidising a pyridine solution of *m*-iodotoluene with chlorine, and forms a white, flocculent mass exploding violently at 200°; Bamberger and Hill (this vol., i, 281) gave 214—221°.

1-Iodosonaphthalene, obtained in an impure state by Willgerodt and Schlösser (this vol., i, 283), melts and evolves gas at 135—145°, and forms an acetate melting and decomposing at 170—175°.

1-Iodoxy*naphthalene* separates from acetic acid as a gelatinous mass which, when dry, explodes at 155°.

T. H. P.

Electrolytic Reduction of Nitro-compounds. By FRITZ HABER (*Zeit. angew. Chem.*, 1900, 433—439).—A summary of results previously obtained (this vol., i, 281, 282). It is pointed out that the process of

electrolytic reduction of nitrobenzene is the same as the ordinary chemical reduction process (compare Bamberger, *Abstr.*, 1894, i, 373, 412; 1896, i, 430; 1898, i, 20, 518, 520, 521; this vol., i, 221).

J. C. P.

Hydrocarbons with High Melting Points from the Last Distillates of Petroleum. By ROMAN ZALOZIECKI and LUDWIG GANS (*Chem. Zeit.*, 1900, 24, 535—536 and 553—557. Compare Prunier, *Ann. Chim. Phys.*, 1879, [v], 16, 28; Divers and Nakamura, *Trans.*, 1885, 47, 925; Boissieu, *Chem. Zeit.*, 1893, 17, 70; Klaudy and Fink, this vol., i, 284).—The authors have isolated a series of hydrocarbons, C_nH_{2n-20} , from crude "petrocene," and to this series they give the name *petrocenes*. The melting points of the products obtained are 250·5°, 228°, 221·5°, 205°, 191·5°, 168°, 155·5°, 153°, 147°, 140°, 216°, 230°, 245—247°. The compound melting at 250·5° has the composition $C_{15}H_{10}$; it yields a *picrate* melting at 178°, and a *bromo-derivative*, $C_{15}H_9Br$, crystallising from benzene in colourless needles and melting at 276°; when reduced with sodium and amyl alcohol, it yields a compound, $C_{15}H_{14}$, melting at 177°.

The compound, $C_{16}H_{12}$, melting at 221·5°, yields a *picrate* melting at 144°, and on reduction gives a *hydrocarbon*, $C_{16}H_{16}$, melting at 185—188°. The compound melting at 205° yields a *picrate* which crystallises in ruby-red prisms melting at 138°, and when reduced gives a hydrocarbon melting at 128—130°.

When treated with various oxidising agents, the hydrocarbons yield no well-defined products; with fuming nitric acid, they yield yellow *nitro-derivatives*.

The *picrates* are most readily formed in chloroform solution and are readily decomposed by all ordinary solvents. The *petrocenes* are not present in crude petroleum, but are formed during the later stages of distillation, and are found in the petroleum resin (Harz). J. J. S.

Amino-derivatives of Methylphloroglucinol. By ARTHUR FRIEDL (*Monatsh.*, 1900, 21, 483—497. Compare *Abstr.*, 1894, i, 22).—*Methylphloramine*, $NH_2 \cdot C_6H_2Me(OH)_2$, obtained when methylphloroglucinol is treated with ammonia in an atmosphere of hydrogen, crystallises in rosettes of yellowish leaflets, melts at 149—150°, and forms a *triacetyl derivative*, which crystallises in short, colourless needles melting at 165—166°; the *hydrochloride* crystallises with H_2O in long, yellowish, monoclinic needles [$a : b : c = 0.9229 : 1 : 0.8815$; $a = 111^\circ 58'$], which melt and decompose at 202°. When phloroglucinol is treated with ethylamine, a *diethyldiaminocresol*, $OH \cdot C_6H_2Me(NHEt)_2$, is obtained; this melts at 124—130°, and forms a *dihydrochloride* crystallising in clusters of greenish needles which melt and decompose at 226—228°. The *bisdiethylammonium* salt of methylphloroglucinol is obtained by the action of diethylamine on methylphloroglucinol. R. H. P.

Compounds of Bismuth with Phenols. By E. RICHARD (*Pharm.*, 1900, [vi], 12, 145—148).—On mixing solutions of a bismuth salt and of an orthodihydric phenol, a citron-yellow, insoluble *derivative* of the type $C_6H_4 \begin{smallmatrix} \diagup O \diagdown \end{smallmatrix} Bi(OH)$ is precipitated; such compounds are

decomposed by sulphuric acid into bismuth sulphate and the parent phenol, whilst nitric acid yields oxidation products of the latter. Hydrochloric acid produces a colourless solution, probably containing a chloride of the type $C_6H_4 \cdot O_2 \cdot BiCl$, but on diluting this is decomposed to form bismuthyl hydroxide. Compounds were prepared from homocatechol, protocatechuic acid, gallic acid, and methyl gallate, but could not be obtained from meta- or para-dihydric phenols. W. A. D.

Action of Benzenediazonium Chloride on Alkaline Solutions of Nitrosophenol. By WALTER BORSCHKE (*Annalen*, 1900, 312, 211—234. Compare this vol., i, 24).—In view of the synthesis by H. B. Hill (this vol., i, 392) of certain compounds described by the author (this vol., i, 24), a more detailed account of the investigation is published.

5-Nitroso-2-hydroxydiphenyl, 5-amino-2-hydroxydiphenyl, diphenylquinone, 5-nitroso-2-hydroxy-1:3-diphenylbenzene, 5-amino-2-hydroxy-1:3-diphenylbenzene, 1:3-diphenylbenzoquinone, and 2:5-dihydroxy-1:3-diphenylbenzene have been already described (*loc. cit.*).

2:5-Dihydroxydiphenyl, $C_{12}H_{10}O_2$, prepared by reducing diphenylquinone with zinc dust and acetic acid, crystallises from dilute alcohol in colourless needles melting at 96—98°. Dianilinophenylbenzoquinone, $CO < \begin{smallmatrix} C(NHPh) : CPh \\ CH = C(NHPh) \end{smallmatrix} > CO$, obtained on heating the quinone with alcoholic aniline, crystallises from glacial acetic acid in black needles with bluish-violet lustre, and melts at 195—196°.

5-Nitro-2-hydroxydiphenyl, $C_{12}H_9O_3N$, produced on oxidising nitrosohydroxydiphenyl with dilute nitric acid, crystallises from 30 per cent. alcohol in yellow needles, and melts at 126—128°; the benzoyl derivative forms colourless needles, and melts at 120°.

Anilindiphenylbenzoquinone, $CO < \begin{smallmatrix} C(NHPh) : CPh \\ CH = CPh \end{smallmatrix} > CO$, prepared from 1:3-diphenylbenzoquinone and alcoholic aniline, separates from hot alcohol as a dark red, crystalline powder melting at 167°.

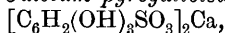
5-Nitroso-2-hydroxy-3-methyldiphenyl, $C_{13}H_{11}O_2N$, obtained by the action of benzenediazonium chloride on nitroso-*o*-cresol, crystallises from dilute acetic acid or aqueous alcohol in yellow leaflets; it melts at 170°, and decomposes at 182—183°. The benzoyl derivative crystallises from a mixture of chloroform and alcohol in slender, pale yellow needles, which melt and darken at 170—172°. M. O. F.

Diphenylmethyl Oxide. By VICTOR AUGER (*Bull. Soc. Chim.*, 1900, [iii], 23, 336—338).—According to Thörner and Zincke (*Abstr.*, 1878, 874), diphenylmethyl oxide [benzhydrol ether], when heated with acetyl chloride, is quantitatively converted into β -benzopinacoline, and must therefore have the composition $\begin{smallmatrix} CPh_2 : C \\ CPh_2 : C \end{smallmatrix} > O$, and not $O(CHPh_2)_2$, as generally supposed. The author is unable to confirm this result, which is attributed to impurities in the materials used by Thörner and Zincke. Moreover, the accuracy of the usual formula is proved by the fact that diphenylmethyl oxide is the only product (besides benzhydrol) of the action of water on diphenylmethyl bromide, and that it is obtained in almost theoretical amount

when a solution of the bromide in light petroleum is treated with zinc oxide in the cold. N. L.

Bromo-derivatives of the Homologous Phloroglucinols. By JOSEF HERZIG, JACQUES POLLAK, and KARL ROHM (*Monatsh.*, 1900, 21, 498—511. Compare this vol., i, 545).—Dibromomethylphloroglucinol with $3\text{H}_2\text{O}$ melts at $112\text{--}115^\circ$, or when anhydrous at $132\text{--}134^\circ$ (compare Boehm, *Abstr.*, 1899, i, 32), and yields a *triacetyl* derivative, which melts at 166° . Dimethylphloroglucinol, when treated with bromine in glacial acetic acid solution, forms a *mono-bromo*-derivative, which crystallises in brown needles, and yields a *triacetyl* derivative melting at 168° . Tribromotrimethylphloroglucinol, $\text{C}_9\text{H}_9\text{O}_3\text{Br}_3$ (compare Boehm, *loc. cit.*), crystallises in monoclinic prisms [$a:b:c=0.9911:1:1.5732$; $\alpha=107^\circ 57'$]; it yields trimethylphloroglucinol when reduced with stannous chloride, and triacetyltrimethylphloroglucinol when treated with acetic anhydride. Trimethylphloroglucinol monomethyl ether, when treated with bromine in glacial acetic acid solution at the ordinary temperature, yields tribromotrimethylphloroglucinol. R. H. P.

Pyrogallolsulphonic Acids. By MARCEL DELAGE (*Compt. rend.*, 1900, 131, 450—453).—*Calcium pyrogallolsulphonate*,



crystallises with $4\text{H}_2\text{O}$ in large, rectangular tablets, and with $5\text{H}_2\text{O}$ in small crystals; both salts are very soluble in water, but are neither deliquescent nor efflorescent. The *barium* salt is a yellowish-white, crystalline powder containing $2\text{H}_2\text{O}$; the *alkali* salts form somewhat large crystals.

The basic calcium salt, $\text{C}_6\text{H}_2(\text{OH})_2 \begin{smallmatrix} \text{O} \\ \diagup \quad \diagdown \\ \text{SO}_3 \end{smallmatrix} \text{Ca} \cdot \text{H}_2\text{O}$, insoluble in water, is obtained by adding calcium carbonate to a hot solution of pyrogallolsulphonic acid. The acid itself is obtained by the action of sulphuric acid of sp. gr. 1.84 on pyrogallol at about 100° .

C. H. B.

Occurrence of Methyl Methylantranilate in Oil of Mandarins. By HEINRICH WALBAUM (*J. pr. Chem.*, 1900, [ii], 62, 135—140).—*Methyl methylantranilate*, $\text{NHMe} \cdot \text{C}_6\text{H}_4 \cdot \text{CO}_2\text{Me}$, was isolated from 'oil of mandarins' (from the fruit of *Citrus madurensis*, Loureiro) by extracting with 25 per cent. sulphuric acid, as an oil which boiled at $130\text{--}131^\circ$ under 13 mm. pressure, and when solidified in a freezing mixture melted at $18.5\text{--}19.5^\circ$. By heating with alcoholic potash, it was converted into methylantranilic acid (Fortmann, *Abstr.*, 1897, i, 301), and thence into methylaniline by heating with hydrochloric acid under pressure; it was also characterised by conversion into acetyl- and dinitro-methylaniline, and nitroso-acetyl- and benzoyl-methylantranilic acids. T. M. L.

Benzoyl Derivatives of Amino-acids formed by the Fission of Proteids. By ALBERT SCHULTZE (*Zeit. physiol. Chem.*, 1900, 29, 467—481. Compare Fischer, *Abstr.*, 1899, i, 888, and this vol., i, 172).—The following benzoyl derivatives were obtained from the corresponding amino-acids by the Schotten-Baumann reaction, using

either sodium or potassium hydroxide; as stated by Fischer, however (*loc. cit.*), they are better prepared by substituting sodium hydrogen carbonate for the basic hydroxide.

Benzoylleucine, obtained from natural leucine, crystallises from water in stout, prismatic needles or leaflets, and melts at 135—140° (Fischer gives 126—128°, footnote, *Ber.*, 1899, 32, 2454); it dissolves in 690 parts of water at 19°, and is inactive in alkaline solution, racemisation probably having occurred in its formation (compare benzoylglutamic acid, *infra*). The *silver*, *lead*, and *zinc* salts crystallise from water, whilst the *potassium* and *barium* salts are very easily soluble in this solvent.

Benzoyl-*L*-aspartic acid melts at 182—183° (Fischer gives 180—181°), and has $[\alpha]_D + 34.8^\circ$ in a solution containing 4 mols. of potassium hydroxide (Fischer found $[\alpha]_D + 37.4^\circ$). The *sodium*, *silver*, *copper* (with 2H₂O), *lead*, and *barium* salts were analysed.

On treating natural, optically active glutamic acid with benzoyl chloride according to the Schotten-Baumann reaction, complete racemisation occurs, and Fischer's racemic benzoylglutamic acid is obtained; the latter, with 1H₂O, melts at 98°, the anhydrous substance melting at 152—154°, as stated by Fischer. The *silver* and *zinc* salts are crystalline, and the *cadmium* and *lead* salts amorphous; the salts of the alkalis and alkaline earths are very soluble in water.

Dibenzoyltyrosine (compare Fischer, footnote cited) crystallises from dilute alcohol in microscopic needles, melts at 211—212°, and yields microcrystalline *potassium* and *cadmium* salts. W. A. D.

Synthesis of Hydroxymethyl-*o*-benzoicsulphinide. By C. MASELLI (*Gazzetta*, 1900, 30, ii, 31—35).—*Hydroxymethyl-*o*-benzoic-sulphinide*, $C_6H_4 \begin{smallmatrix} \text{CO} \\ \text{SO}_2 \end{smallmatrix} N \cdot CH_2 \cdot OH$, prepared by heating *o*-benzoic-sulphinide with formaldehyde, separates from alcohol in prismatic crystals, which are insoluble in water and melt and partially decompose at 225°. It reduces ammoniacal silver nitrate solution only in presence of potassium hydroxide, and gives no coloration with magenta and sulphuric acid. T. H. P.

2-Chloro-3-hydroxybenzoic and 2:6 Dichloro-3-hydroxybenzoic Acids. By GIROLAMO MAZZARA and V. BERTOZZI (*Gazzetta*, 1900, 30, ii, 84—94).—By the action of sulphuryl chloride on ethyl *m*-hydroxybenzoate, two ethyl chlorohydroxybenzoates are formed, one corresponding with an acid melting at 178°, of the constitution $[CO_2H : OH : Cl = 1 : 3 : 6]$ and the other with an acid melting at 156—157° (see Abstr., 1899, i, 810); the latter acid is now shown to have the constitution $[CO_2H : OH : Cl = 1 : 3 : 2]$.

2:6-Dichloro-3-hydroxybenzoic acid, $C_7H_4O_3Cl_2$, prepared by the action of sulphuryl chloride on ethyl or methyl 6-chloro-3-hydroxybenzoate or on ethyl 2-chloro-3-hydroxybenzoate, crystallises with 1 mol. H₂O in very short, doubly-refracting prisms melting at 122—124°; its aqueous solution gives a violet coloration with ferric salts. The *dimethyl* ester, $C_9H_8O_3Cl_2$, separates from dilute alcohol in elongated, hexagonal prisms, and from light petroleum in large crystals melting at 57°. The positions of the chlorine atoms in the molecule (one on

either side of the carboxyl radicle) is shown by the fact that the acid cannot be methylated by hydrochloric acid in presence of methyl alcohol.

T. H. P.

Isomerism of the Formylphenylacetic Esters. By WILHELM WISLICENUS (*Annalen*, 1900, 312, 34—64. Compare Abstr., 1896, i, 552).—On applying to the formylphenylacetic esters the method of determining constitution elaborated by Drude (Abstr., 1897, ii, 537), which depends on the absorption of rapidly oscillating electrical vibrations, it is found that the latter are strongly absorbed by the α -ester, having the enolic structure $\text{OH}\cdot\text{CH}\cdot\text{CPh}\cdot\text{CO}_2\text{Et}$; concurrently with transformation into the β -modification, the absorption decreases, and becomes very slight by the time the liquid has solidified, showing that the α -ester changes spontaneously into the isomeride.

In the previous paper on this subject, it was stated that both esters yield the same benzoate, $\text{OBz}\cdot\text{CH}\cdot\text{CPh}\cdot\text{CO}_2\text{Et}$, which melts at $87-88^\circ$. It is now found that by varying the conditions under which this substance is produced, two geometrical isomerides may be obtained.

The α -benzoate, $\text{OBz}\cdot\text{CH}\cdot\text{CO}_2\text{Et}\cdot\text{CPh}$, produced when the sodium derivative of

ethyl hydroxymethylphenylacetate is suspended in cooled ether and treated with benzoyl chloride (1 mol.), is a viscous, colourless oil, which boils at $245-246^\circ$ under 18 mm. pressure, when it becomes

converted into the β -benzoate, $\text{OBz}\cdot\text{CH}\cdot\text{Ph}\cdot\text{C}\cdot\text{CO}_2\text{Et}$, melting at $87-88^\circ$;

the latter has been already described (*loc. cit.*), and is formed when the sodium derivative of the ester is dissolved in water preparatory to treatment with benzoyl chloride. Both modifications yield the dibromide which melts at $66-67^\circ$.

The α -m-nitrobenzoate, $\text{NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{CO}_2\cdot\text{CH}\cdot\text{CO}_2\text{Et}\cdot\text{CPh}$, crystallises from ether in monoclinic prisms [$a:b:c = 1.8752:1:1.9744$; $\beta = 100^\circ 47'$], melts at $101-102^\circ$, and boils at $287-288^\circ$ under 23 mm. pressure.

The β -m-nitrobenzoate, $\text{NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{CO}_2\cdot\text{CH}\cdot\text{Ph}\cdot\text{C}\cdot\text{CO}_2\text{Et}$, crystallises from ethyl

acetate in short, triclinic prisms [$a:b:c = 1.3842:1:0.6140$. $\alpha = 90^\circ 42'$; $\beta = 112^\circ 34'$; $\gamma = 88^\circ 30'$], and melts at $117-118^\circ$. Repeated distillation converts the α -modification into the isomeride, and the same result is achieved when the substance is heated at $200-220^\circ$ during 1 hour; bromine transforms both isomerides into a vaseline-like substance.

The paper concludes with some remarks on the constitution of metallic derivatives of tautomeric substances; it is suggested that the metallic derivatives of ethyl formylphenylacetate are geometrically isomeric.

M. O. F.

Synthesis of β -p-isoPropylphenyl- α -methylhydracrylic Acid. By P. GRIGOROWITSCH (*J. Russ. Phys. Chem. Soc.*, 1900, 32, 324—327).—By acting with zinc and ethyl α -bromopropionate on cuminaldehyde and saponifying the ester thus formed, β -p-iso-propylphenyl- α -methylhydracrylic acid, $\text{C}_6\text{H}_4\text{Pr}^\beta\cdot\text{CH}(\text{OH})\cdot\text{CHMe}\cdot\text{CO}_2\text{H}$, is obtained; it

is almost insoluble in water or benzene, but dissolves in ether or alcohol, and separates from the last-named solvent in the form of hexagonal crystals melting at 123° . The *potassium* and *lithium* salts deliquesce in the air; the *sodium* salt (with $2\frac{1}{2}\text{H}_2\text{O}$) crystallises in thin scales; the *barium* salt (with $4\text{H}_2\text{O}$) is soluble in alcohol and slightly so in water, the *calcium* salt (with $3\frac{1}{2}\text{H}_2\text{O}$) having similar properties.

By distilling the acid with sulphuric acid (1 part to 4 of water), *p*-isopropylallylbenzene is obtained, whilst on heating the acid in sealed tubes with hydriodic acid at 100° a molecule of water is removed from the molecule and α -methyl-*p*-isopropylcinnamic acid, $\text{C}_6\text{H}_4\text{Pr}^{\beta}\cdot\text{CH}:\text{CMe}\cdot\text{CO}_2\text{H}$, formed; the latter separates from aqueous alcohol in beautiful, acicular crystals melting at 90° . T. H. P.

Products of Condensation of Dichlorophthalic Anhydride with Diethylaniline. By ÉMILE SEVERIN (*Bull. Soc. Chim.*, 1900, [iii], 23, 686—693. Compare this vol., i, 296, 450).—3 : 4-Dichloro-2'-diethylaminobenzoylbenzoic acid, $\text{NEt}_2\cdot\text{C}_6\text{H}_4\cdot\text{CO}\cdot\text{C}_6\text{H}_2\text{Cl}_2\cdot\text{CO}_2\text{H}$, obtained by the interaction of 3 : 4-dichlorophthalic anhydride with diethylaniline in the presence of aluminium chloride, crystallises in brilliant scales melting at 185° . The *acetate*, or *mixed anhydride*, $\text{NEt}_2\cdot\text{C}_{13}\text{H}_6\text{OCl}_2\cdot\text{CO}\cdot\text{OAc}$, crystallises from boiling benzene or alcohol in colourless scales melting at 130° . The *methyl* ester, obtained by the action of sodium methoxide on the preceding compound, crystallises in tufts of slender needles melting at 152° , whilst the *ethyl* ester crystallises in yellow needles melting at 145° .

The preparation of 3 : 4-dichloro-2'-diethylaminobenzoylbenzoic acid and of the dialkylaminodichloroanthraquinones has already been described (this vol., i, 450). N. L.

***p*-Toluoyle-*p*-benzoic Acid and *pp*-Benzophenonedicarboxylic Acid.** By HEINRICH LIMPRICHT (*Annalen*, 1900, 312, 91—98. Compare Abstr., 1898, i, 322, and this vol., i, 31).—*p*-Toluoyle-*p*-benzoic acid, $\text{C}_6\text{H}_4\text{Me}\cdot\text{CO}\cdot\text{C}_6\text{H}_4\cdot\text{CO}_2\text{H}$, prepared by oxidising *pp*-ditolyl ketone with chromic acid in glacial acetic acid solution, crystallises from alcohol in aggregates of silky leaflets, and melts at 228° ; the *barium* and *silver* salts are anhydrous, and the *methyl* ester crystallises in long needles melting at 126° . The *chloride* melts at 110° , and the *amide* at 196° .

Phenylene ditolyl diketone, $\text{C}_6\text{H}_4\text{Me}\cdot\text{CO}\cdot\text{C}_6\text{H}_4\cdot\text{CO}\cdot\text{C}_6\text{H}_4\text{Me}$, obtained by heating the chloride of the foregoing acid with aluminium chloride in toluene, crystallises from acetone in six-sided, rhombic plates melting at 188° .

Toluoylecarbinolbenzoic acid, $\text{C}_6\text{H}_4\text{Me}\cdot\text{CH}(\text{OH})\cdot\text{C}_6\text{H}_4\cdot\text{CO}_2\text{H}$, formed when toluoylebenzoic acid is reduced with zinc dust and ammonia, crystallises from hot water in colourless, triclinic leaflets containing $\frac{1}{2}\text{H}_2\text{O}$; it melts at 161.5° , and yields a crystalline *silver* salt.

Benzophenone-4 : 4'-dicarboxylic acid, $\text{CO}(\text{C}_6\text{H}_4\cdot\text{CO}_2\text{H})_2$, produced when oxidising *pp*-ditolyl ketone to *p*-toluyl-*p*-benzoic acid, is separated from the latter in the form of potassium salt; it forms a white, crystalline powder which dissolves with difficulty in alcohol, ether, acetone,

or benzene, and melts above 360° . The acid obtained by Zincke and Weber (this Journal, 1875, 155) on oxidising dibenzyltoluene is probably identical with this compound, which has been already described by Ador and Crafts (Abstr., 1878, 405); the *silver* salt is anhydrous, and the *methyl* ester crystallises from acetone in white leaflets and melts at 224° . The *chloride* separates from toluene in rhombic crystals melting at 133° , and the *amide*, which forms slender, white needles, melts at 300° .

pp-Benzhydrophtallic acid, $\text{OH}\cdot\text{CH}(\text{C}_6\text{H}_4\cdot\text{CO}_2\text{H})_2$, prepared by reducing benzophenone-4:4'-dicarboxylic acid with zinc dust and ammonia, crystallises from water in small, colourless needles, and melts at 286° . M. O. F.

o-Xylylphthaloylic Acid and Phthaloylphthalic Acid. By HEINRICH LIMPRICHT (*Annalen*, 1900, 312, 99—109).—*o-Xylylphthaloylic* acid*, $\text{C}_6\text{H}_3\text{Me}_2\cdot\text{CO}\cdot\text{C}_6\text{H}_4\cdot\text{CO}_2\text{H}$, prepared by the action of aluminium chloride on a mixture of phthalic anhydride, *o*-xylene, and carbon disulphide, crystallises from alcohol in aggregates of colourless needles and thin plates melting at 162° . The *chloride* melts at 113 — 114° , and the *acetanhydride*, $\text{C}_6\text{H}_3\text{Me}_2\cdot\text{CO}\cdot\text{C}_6\text{H}_4\cdot\text{CO}\cdot\text{OAc}$, produced on heating the acid with acetic anhydride, separates from alcohol in monoclinic crystals melting at 102° .

Tolylxylylphthalide, $\text{CO}\langle\text{C}_6\text{H}_4\rangle_{\text{O}}\text{C}(\text{C}_6\text{H}_4\text{Me})\cdot\text{C}_6\text{H}_3\text{Me}_2$, formed when *o*-xylylphthaloylic chloride is heated with aluminium chloride and toluene in carbon disulphide, is also produced from *p*-toluoyl-*o*-benzoic chloride and *o*-xylene.

o-Xylylphthalide, $\text{CO}\langle\text{C}_6\text{H}_4\rangle_{\text{O}}\text{CH}\cdot\text{C}_6\text{H}_3\text{Me}_2$, obtained by reducing xylylphthaloylic acid with zinc dust and hydrochloric acid, crystallises from alcohol in small, white needles and melts at 138° .

o-Dimethyl-o-benzylbenzoic acid, $\text{C}_6\text{H}_3\text{Me}_2\cdot\text{CH}_2\cdot\text{C}_6\text{H}_4\cdot\text{CO}_2\text{H}$, the final product of reduction of xylylphthaloylic acid, separates from alcohol in highly refractive crystals and melts at 134° ; the *silver* salt is amorphous.

o-Dimethylantranol, $\text{C}_6\text{H}_4\langle\text{C}(\text{OH})\text{CH}\rangle\text{C}_6\text{H}_2\text{Me}_2$, produced by the action of concentrated sulphuric acid on dimethylbenzylbenzoic acid, crystallises from alcohol in small, yellow needles and melts at 149° .

o-Dimethylantraquinone, $\text{C}_6\text{H}_4\langle\text{CO}\rangle_{\text{CO}}\text{C}_6\text{H}_2\text{Me}_2$, an oxidation product of the foregoing substance, sublimes in long, yellow needles melting at 200° .

Phthaloylphthalic acid, $\text{C}_6\text{H}_3(\text{CO}_2\text{H})_2\cdot\text{CO}\cdot\text{C}_6\text{H}_4\cdot\text{CO}_2\text{H}$, prepared by oxidising *o*-xylylphthaloylic acid in alkaline solution with potassium permanganate, separates from dilute alcohol in the form of a white, crystalline powder containing $1\text{H}_2\text{O}$, and in the anhydrous condition melts at 189° . The *ammonium* salt is deliquescent, the *barium* salt

* The expression *phthaloyl* is employed to represent the group $\text{CO}_2\text{H}\cdot\text{C}_6\text{H}_4\cdot\text{CO}$.

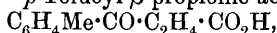
contains $8\text{H}_2\text{O}$, and the *silver* salt is anhydrous; the *methyl* ester and the *chloride* are indefinite compounds.

Phthaloylphthalic anhydride, $\text{CO}_2\text{H}\cdot\text{C}_6\text{H}_4\cdot\text{CO}\cdot\text{C}_6\text{H}_3\begin{smallmatrix} \diagup \text{CO} \\ \diagdown \text{CO} \end{smallmatrix}\text{O}$, separates from benzene in crystalline aggregates melting at 175° ; the *imide*, which has perhaps the constitution $\text{NH}_2\cdot\text{CO}\cdot\text{C}_6\text{H}_4\cdot\text{CO}\cdot\text{C}_6\text{H}_3\begin{smallmatrix} \diagup \text{CO} \\ \diagdown \text{CO} \end{smallmatrix}\text{NH}$, is obtained by heating ammonium phthaloylphthalate at 220° and melts at 246° .

Phthaloyltoluoylbenzoic acid,

$\text{CO}_2\text{H}\cdot\text{C}_6\text{H}_4\cdot\text{CO}\cdot\text{C}_6\text{H}_3(\text{CO}_2\text{H})\cdot\text{CO}\cdot\text{C}_6\text{H}_4\text{Me}$, prepared by heating phthaloylphthalic anhydride with toluene and aluminium chloride, decomposes at 86° , with previously melting; the *silver* and *barium* salts are anhydrous. M. O. F.

p-Toluoyl- β -propionic Acid. By HEINRICH LIMPRICHT (*Annalen*, 1900, 312, 110—117).—*p*-Toluoyl- β -propionic acid,

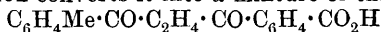


prepared from succinic anhydride and toluene under the influence of aluminium chloride, has been already described by Claus and by Burkner; the *methyl* ester forms silky needles and melts at 43° , whilst the *amide* crystallises in white leaflets having a bluish glance, and melts at 160° .

Tolylpyridazinone, $\text{C}_6\text{H}_4\text{Me}\cdot\text{C}\begin{smallmatrix} \diagup \text{CH}_2\cdot\text{CH}_2 \\ \diagdown \text{N}-\text{NH} \end{smallmatrix}\text{CO}$, prepared by heating the sodium salt of the foregoing acid with aqueous hydrazine (compare Gabriel and Colman, *Abstr.*, 1899, i, 390), crystallises from alcohol and melts at 147° .

Propiophenonedicarboxylic acid, $\text{CO}_2\text{H}\cdot\text{C}_2\text{H}_4\cdot\text{CO}\cdot\text{C}_6\text{H}_4\cdot\text{CO}_2\text{H}$, obtained on oxidising a very dilute, aqueous solution of toluyl- β -propionic acid with potassium permanganate, crystallises from hot water, and sinters at 246° without melting definitely; the *barium* and *silver* salts are anhydrous.

Succitoyl ketone (*ditoyl ethylene diketone*), $\text{C}_2\text{H}_4(\text{CO}\cdot\text{C}_6\text{H}_3\text{Me})_2$, one of the products of the action of aluminium chloride on succinic chloride and toluene, crystallises from alcohol in colourless needles and melts at 161° ; oxidation converts it into a mixture of the acids



and $\text{C}_2\text{H}_4(\text{CO}\cdot\text{C}_6\text{H}_4\cdot\text{CO}_2\text{H})_2$.

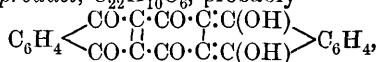
Ditoylsuccinide, $\text{CO}\begin{smallmatrix} \diagup \text{C}_2\text{H}_4 \\ \diagdown \text{O} \end{smallmatrix}\text{C}(\text{C}_6\text{H}_4\text{Me})_2$, produced in association with succitoyl ketone, crystallises from dilute alcohol in lustrous, six-sided leaflets and melts at $156\text{--}157^\circ$; the *sodium* and *barium* salts are crystalline. M. O. F.

Thermal Study of Protocatechuic or 3:4-Dihydroxybenzoic Acid. Influence of Phenolic Hydroxyl. By GUSTAVE MASSOL (*Bull. Soc. Chim.*, 1900, [iii], 23, 331—333. Compare *Abstr.*, 1899, ii, 353).—Carefully purified protocatechuic acid crystallises in tufts of yellow, prismatic needles melting at 199° . It is neutralised by 1.5 mols. of alkali when phenolphthalein is used as the indicator, whilst with litmus 2 mols. are required. The general acidity is therefore increased

by the presence of the hydroxyl groups, but nevertheless the heats of neutralisation for the first, second, and third equivalents of alkali (12.9, 7.6, and 0.1 Cals. respectively) are somewhat less than the corresponding values for *m*- and *p*-hydroxybenzoic acids which contain one hydroxyl group less. The heat of dissolution of anhydrous protocatechuic acid is -5.82 Cal. The heat of formation of the sodium salt is 17.69 Cal., all the substances concerned being in the solid state, and its heat of dissolution is $+0.64$ Cal. The former value is practically identical with the heats of formation of the sodium salts of benzoic, *m*-hydroxybenzoic, and *p*-hydroxybenzoic acids, thus confirming the conclusion that the phenolic hydroxyl is without influence on the acidimetric value of the carboxyl group, except when in the ortho-position with respect to the latter. N. L.

Orthocarboxylic Acids and other Derivatives of 1:2- and 1:4-Dihydroxynaphthalene. By FRIEDRICH RUSSIG (*J. pr. Chem.*, 1900, [ii], 62, 30—60).—1:4-Dihydroxynaphthalene-2-carboxylic acid, prepared by heating sodium 1:4-dihydroxynaphthalene with carbon dioxide under pressure at 170° , crystallises from dilute alcohol in monoclinic needles, and from acetic acid in monoclinic tablets or prisms containing 1 mol. of acetic acid, and melts at 186° with evolution of carbon dioxide. The *monoacetyl* derivative forms colourless, rhombic plates, and melts at 193° with evolution of gas. The *monomethyl ether*, $\text{OH} \cdot \text{C}_{10}\text{H}_5(\text{OMe}) \cdot \text{CO}_2\text{H}$, crystallises from acetic acid, melts at 178° , and is converted quantitatively into hydroxymethoxynaphthalene; its *methyl ester*, $\text{OH} \cdot \text{C}_{10}\text{H}_5(\text{OMe}) \cdot \text{CO}_2\text{Me}$, crystallises from dilute methyl alcohol in hexagonal needles and melts without decomposition at 134° ; the *acetyl* derivative, $\text{OAc} \cdot \text{C}_{10}\text{H}_5(\text{OMe}) \cdot \text{CO}_2\text{H}$, crystallises from alcohol in felted needles, and melts with decomposition at 172° . The *ethyl ether*, $\text{OH} \cdot \text{C}_{10}\text{H}_5(\text{OEt}) \cdot \text{CO}_2\text{H}$, crystallises from acetic acid in stout prisms, from alcohol in needles, and melts at 170° with formation of hydroxyethoxynaphthalene; its *ethyl ester* crystallises in hexagonal prisms, and melts at 98° . The acid is converted by stannic chloride into β -chloro- α -naphthaquinone, and its constitution is thus established; the methyl and acetyl groups probably enter in the meta-position to the carboxyl.

A *condensation product*, $\text{C}_{22}\text{H}_{10}\text{O}_6$, probably



in which one naphthalene group has been oxidised from the quinol to the quinone, is formed in the preparation of the acid; it crystallises from aniline in yellow needles, melts above 350° , sublimes without decomposition, and forms an orange-coloured sodium salt; the *diacetyl* derivative crystallises from nitrobenzene or xylene in yellow needles, sublimes at about 260° , and melts when quickly heated above 300° . By warming the acid with sulphuric acid, a *condensation product*, $\text{C}_{22}\text{H}_8\text{O}_6$, is produced, which crystallises from aniline or nitrobenzene in yellow needles, contains no hydroxyl group, and is regarded as

$\text{C}_6\text{H}_4 \begin{array}{c} \text{CO} \cdot \text{C} \cdot \text{CO} \cdot \text{C} \cdot \text{CO} \\ | \quad | \\ \text{CO} \cdot \text{C} \cdot \text{CO} \cdot \text{C} \cdot \text{CO} \end{array} \text{C}_6\text{H}_4$; sulphonic acids are also produced. By

distilling with zinc dust, the condensation product is reduced to *dinaphthanthracene*, $C_{22}H_{14}$, which forms yellowish flakes with a green fluorescence.

1-*Hydroxy-4-methoxynaphthalene* forms long, colourless needles, and melts at 125° . 1:4-*Dimethoxynaphthalene* crystallises from carbon disulphide in monosymmetric needles, and melts at 85° . 1-*Hydroxy-4-ethoxynaphthalene* crystallises from water in colourless needles and melts at 90° . Methoxynaphthol readily yields an *oxidation product*, $C_{22}H_{16}O_4$, which crystallises from pyridine or acetic acid in blue prisms, can be used as a dye in the same way as indigo, and is regarded

as $OMe \cdot C \begin{array}{c} \diagup CH \\ \diagdown C_6H_4 \end{array} - C \begin{array}{c} \diagup \\ \diagdown \end{array} - C \begin{array}{c} \diagdown CH \\ \diagup C_6H_4 \end{array} \cdot C \begin{array}{c} \diagup \\ \diagdown \end{array} \cdot OMe$; the ethyl ether gives a similar compound.

A bye-product in the preparation of the acid, which crystallises in minute, colourless needles and melts at about 280° , is regarded as the dicarboxylic acid.

1:2-*Dihydroxynaphthalene-3-carboxylic acid* separates from dilute alcohol in yellow crystals, and melts at 215° with evolution of carbon dioxide; the *diacetyl* derivative crystallises from dilute acetic acid in colourless needles and begins to decompose and melt at 185° . The *dicarboxylic acid* is produced when the naphthol is heated with carbon dioxide at 200° .
T. M. L.

Double Compounds of Aromatic Aldehydes and Esters with Orthophosphoric Acid. By P. N. RAIKOW (*Chem. Zeit.*, 1900, 24, 367—368).—Klages has shown (*Abstr.*, 1898, i, 477; 1899, i, 598) that by the action of phosphoric acid on certain aromatic ketones well-crystallised double compounds are produced. The author has obtained similar substances by the combination of phosphoric acid with aromatic aldehydes in which the aldehyde group is directly attached to the benzene nucleus; thus, benzaldehyde and anisaldehyde readily unite with phosphoric acid, whilst formaldehyde, acetaldehyde, valeraldehyde, heptaldehyde, cinnamaldehyde, and cuminaldehyde do not react with it.

If one or both of the hydrogen atoms occupying the *o*-positions in the aldehyde molecule are replaced by radicles, the aldehyde loses its power of combining with phosphoric acid; in this respect, the behaviour of the aldehydes differs from that of the ketones, which only fail to react with phosphoric acid when both the hydrogen atoms in the *o*-position have undergone substitution. If, on the other hand, the hydrogen atom in the *p*-position is replaced, the activity is not affected. Anisaldehyde, for example, unites very readily with phosphoric acid to form a crystalline compound, whilst salicylaldehyde does not combine with it under any conditions.

The ability of aldehydes to react with phosphoric acid is dependent, not only on the position, but also on the chemical nature of the substituting radicles; this is shown by the fact that none of the three isomeric nitrobenzaldehydes combines with this acid, whilst, as previously stated, anisaldehyde does so readily.

Benzoyl chloride and ethyl benzoylacetate do not react with phos-

phoric acid; methyl benzoate combines with it readily to form a colourless, crystalline substance, but the higher esters of benzoic acid and methyl and ethyl salicylates are without action.

By means of experiments with a number of substances which do not contain a carbonyl group, such as benzonitrile, toluonitrile, benzyl chloride and iodide, and benzyl alcohol, the author has proved that the activity of the aldehydes, ketones, and esters towards phosphoric acid is entirely dependent on the carbonyl group which is directly attached to the benzene nucleus. When benzyl alcohol is warmed with phosphoric acid, a stable compound separates as an oil; this is probably a benzyl phosphate. E. G.

Vanillin in Vinegar-essences. By AUG. LUDWIG FROBENIUS (*Chem. Zeit.*, 1900, 24, 369).—In a sample of a vinegar-essence, the author has found traces of a terpene, and also a substance which yields vanillin on oxidation and is probably coniferin (compare Stocký, this vol., ii, 454). E. G.

Synthesis of Benzene by the Action of Zinc Ethyl on Acetophenone. By MAURICE DELACRE (*Chem. Centr.*, 1900, ii, 255; from *Bull. Acad. roy. Belg.*, 1900, [iii], 39, 64—68. Compare *ibid.*, 1896, [iii], 32, 446).—From the alcoholic mother liquors of α -homodypnopinacone, in addition to γ -dypnopinacolin, γ -homodypnopinacone, $C_{32}H_{28}O_2$, has also been isolated. It crystallises from glacial acetic acid in lustrous, heavy needles, melts at 205° , is not attacked by prolonged boiling with glacial acetic acid, but when boiled with acetyl chloride forms nodules and silky needles of a substance which melts at 146° (α -homodypnopinacolin?). A diagram is given showing the compounds formed in the conversion of acetophenone into triphenylbenzene. E. W. W.

Gradual Synthesis of the Benzene Ring. By MAURICE DELACRE (*Chem. Centr.*, 1900, ii, 255—256; from *Bull. Acad. roy. Belg.*, 1900, [iii], 39, 68—87).—From a determination of the quantity of zinc ethyl which is required to convert dypnone into dypnopinalcolene, $C_{32}H_{26}$, it is evident that dypnone is first polymerised to dypnopinacone before forming the hydrocarbon, and that in the first change the zinc ethyl does not act as a reducing agent. Similarly, in the synthetical formation of triphenylbenzene from acetophenone, dypnone undergoes a like polymerisation. The reverse change is also easily effected, for by distilling dypnopinacone under 20 mm. pressure a good yield of almost pure dypnone boiling at 270° is obtained. Moreover, Gesché has found (compare following abstract) that by the action of alcoholic potash on dypnone, dypnopinacone is formed, and that this is then easily decomposed into α -dypnopinacolin. Polymerisation is also brought about by heating dypnone with potassium cyanide at 160° , although there is no action at 110° .

From the products obtained by heating dypnone for 8 days at 225 — 230° , not only ethylbenzene, but also the polymeride of allylbenzene boiling at above 320° has been isolated (compare Errera, *Gazzetta*, 1884, 14, 504). When dry dypnopinalcolene, $C_{32}H_{26}$, is distilled, triphenylbenzene and a hydrocarbon boiling at about 340° are formed. The latter is probably identical with that obtained from dypnone.

The formation of reduction products such as dypnopinacolin alcohol, $C_{32}H_{28}O$, and dypnopinalcolene, $C_{32}H_{26}$, in the distillation of dypnone is accompanied also by simultaneous oxidation, benzoic acid and diphenylfurfuraldehyde being formed.

E. W. W.

Action of Potassium Hydroxide on Dypnone. By LOUIS GESCHÉ (*Chem. Centr.*, 1900, ii, 256—257; from *Bull. Acad. roy. Belg.*, 1900, 293—313).—By heating dypnone with alcoholic potash in a sealed tube, triphenylbenzene is formed, but this is really the result of secondary reactions, for if the mixture be heated in an open flask at 180° , benzoic acid and a hydrocarbon, $C_{25}H_{22}$, are the final products. The action takes place in three phases. The dypnopinacone first formed is converted into α -isodypnopinacolin, $C_{32}H_{26}O$, by elimination of water, and this is finally decomposed by the action of the alkali, forming benzoate and the hydrocarbon. The hydrocarbon, $C_{25}H_{22}$, crystallises in white leaflets, becomes greenish on exposure to light, melts at 95° , is soluble in alcohol, and when reduced with sodium amalgam yields the hydrocarbon $C_{25}H_{24}$, which separates in large crystals and melts at 144° . α -isodypnopinacolin, $C_{32}H_{26}O$, prepared by the action of alcoholic potash on dypnone at the ordinary temperature, crystallises from glacial acetic acid or hot alcohol, and melts at 131.5 — 132° . Since α -homodypnopinacolin, melting at 130° , was isolated, homodypnopinacone is probably also a product of the action of alcoholic potash at the ordinary temperature. Dypnopinacone, $C_{32}N_{23}O_2$, obtained by the action of the alkali on dypnone for 3 hours, crystallises from ether and alcohol in white needles and melts at 162° ; when dissolved in hot glacial acetic acid, it forms isodypnopinacolin.

E. W. W.

Isomerism in the Menthol Series. III. By IWAN L. KONDAKOFF and E. LUTSCHININ (*J. pr. Chem.*, 1900, [ii], 62, 1—30. Compare this vol. i, 104).—The variations in the physical constants of fenchyl alcohol are probably due to partial racemisation, and this view has been confirmed by the isolation, from the crude reduction-product of *d*-fenchone, of a liquid which solidifies on cooling, boils at 199° (fenchyl alcohol boils at 201°), and is feebly dextrorotatory. The action of phosphorus pentachloride on fenchyl alcohol gives an impure chloride containing fenchene; a much purer product is obtained by heating the alcohol on a water-bath with concentrated hydrochloric acid; at higher temperatures, a *dichloride* is produced, in which the diagonal bond is probably broken. By the action of alcoholic potash on the chloride at 100° , there is produced along with the fenchene a *secondary fenchyl chloride*, $C_{10}H_{17}Cl$, which crystallises from alcohol, melts at 79 — 80° , has $[\alpha]_D +16^\circ33'$, does not react with moist silver oxide, and resembles bornyl chloride in its odour and other properties; at 150° , only fenchene is produced. Crude fenchyl chloride appears, therefore, to be a mixture of the solid secondary chloride with a much larger amount of a tertiary chloride, probably liquid, which is much more easily decomposed by alcoholic potash, and is formed as the result of an isomeric change similar to that which takes place in the case of menthol and carvomenthol (Kondakoff and Lutschinin, *loc. cit.*). Fenchene hydrochloride closely resembles fenchyl chloride, and is probably almost all tertiary;

moist silver oxide converts it into Bertram and Helle's *isofenchyl* alcohol (this vol., i, 398).

Fenchyl bromide, prepared by the action of cold hydrobromic acid on *l*-fenchyl alcohol from *d*-fenchone, boils at 92–96° under 11 mm. pressure, has a sp. gr. 1.2368 at 19.5°/19.5°, n_D 1.4988, $[\alpha]_D$ –43°17'. A small amount of a *dibromide* is also produced, which crystallises from alcohol and melts at 49°. *Fenchene hydrobromide* resembles fenchene bromide, but gave $[\alpha]_D$ –27°16'.

By the action of alcoholic potash on fenchyl bromide, and to a less extent on the chloride, a fenchene of low boiling point is produced, and it is suggested that the product contains at least two isomerides.

T. M. L.

Sesquiterpene of Oil of Ginger. By HUGO VON SODEN and WILHELM ROJAHN (*Chem. Centr.*, 1900, ii, 97; from *Pharm. Zeit.*, 45, 414–415).—The sesquiterpene, *zingiberene*, $C_{15}H_{24}$, which is the main constituent of oil of ginger, is a colourless, almost odourless oil easily soluble in ether, light petroleum, benzene, or absolute alcohol; it boils at 269–270°, or at 134° under 14 mm. pressure, has a sp. gr. 0.872 at 15° and a rotatory power of –69° (100 mm. tube). The hydrogen chloride and hydrogen bromide additive compounds and the tetrabromide are liquids. It forms neither a nitrosochloride nor a nitrosate.

The lower fractions of oil of ginger contain small quantities of aldehyde-like substances (fatty aldehydes?).

E. W. W.

Natural Resins [Ueberwallungsharze]. VI. Dry Distillation of Lariciresinol. By MAX BAMBERGER and EMIL VISCHNER (*Monatsh.*, 1900, 21, 564–570. Compare *Abstr.*, 1899, i, 929).—Lariciresinol, when subjected to dry distillation, yields guaicol, pyroguaiacin, and an undetermined compound melting at 140°, together with carbon dioxide and gaseous hydrocarbons.

R. H. P.

Constitution of β -isoCinchonine. By ZDENKO HANNS SKRAUP [and in part H. COPONY and G. MEDANICH] (*Monatsh.*, 1900, 21, 512–534. Compare *Abstr.*, 1899, i, 960).— β -isoCinchonine, when treated with hydrogen bromide, yields hydrobromocinchonine, does not react with phenylhydrazine, and, when treated with methyl iodide, yields a methiodide which melts at 232.5° (not 253° as given by Jungfleisch and Léger, *Abstr.*, 1888, i, 380). By treatment of β -iso-cinchonine hydriodide with methyl iodide, an isomeric *methiodide*, which is an unstable oil, is obtained, thus showing that β -isocinchonine, like cinchonine, is a double tertiary base. β -isoCinchonine acid sulphate, which crystallises with $4\frac{1}{2}H_2O$ (not $4H_2O$, compare Hesse, *Abstr.*, 1891, i, 584), when heated at 140°, is transformed into β -iso- ψ -cinchon-icine, $C_{19}H_{22}ON_2$, which is not of ketonic character like the analogous cinchonidine (cinchotoxine) obtained by heating cinchonine acid sulphate. When oxidised with chromic acid, β -isocinchonine yields carbon dioxide, formic and cinchonic acids, and β -isomerochinene [β -isomeroquinene], $C_{19}H_{15}O_2N$, an amorphous optically active base isomeric with meroquinene, which is obtained from cinchonine in a similar manner

(Koenigs, Abstr., 1894, i, 392). These reactions show that the quinoline portion of the cinchonine molecule is not affected when it is transformed to *β*-isocinchonine.

The following new compounds and properties are described: *β*-isocinchonine hydrochloride dissolves in about 50 parts of water, the hydriodide crystallises with H_2O in needles, and melts at 217° ; hydrobromocinchonine dissolves in 250—270 parts of absolute alcohol, and its dihydrobromide in about 60 parts of water; the *hydriodide*, $C_{19}H_{22}ON_2, MeI, HI$, of the unstable, oily *β*-isocinchonine methiodide, which crystallises in yellow needles, turns dark red when heated, sinters at 190° , and melts at 196° ; *β*-iso-*ψ*-cinchonine hydrochloride, $C_{19}H_{22}ON_2, HCl$, which forms compact crystals, with $3H_2O$, and is soluble in 2 parts of water; the *hydriodide*, which crystallises in prisms, with $2H_2O$, and is slightly soluble in water; the *dihydriodide*, which crystallises in yellow prisms, with $3H_2O$, melts at 163.5 — 165° , and is easily soluble in water; *β*-isomeroquininine aurichloride, $C_9H_{15}O_2N, HAuCl_4$, which crystallises in prisms, melts and decomposes at about 180° .
R. H. P.

α- and *β*-Isocinchonine. By ZDENKO H. SKRAUP and RUD. ZWERGER (*Monatsh.*, 1900, 21, 535—563. Compare preceding abstract and Abstr., 1899, i, 960).—*α*- and *β*-isocinchonine resemble cinchonine in that their acid sulphates undergo molecular transformation when heated; thus *β*-isocinchonine sulphate yields *β*-iso-*ψ*-cinchonine (*loc. cit.*), and *α*-isocinchonine sulphate yields two isomeric bases, namely, *α*-isocinchonine, which is of a ketonic nature, and *α*-iso-*ψ*-cinchonine, which is an amorphous substance melting at 73 — 74° and does not react with phenylhydrazine. Neither *α*-isocinchonine nor *β*-isocinchonine react with phosphorus pentachloride, acetic anhydride, benzoyl chloride, phenylcarbimide, or phenylhydrazine. *α*-isocinchonine, like *β*-isocinchonine (*loc. cit.*), when oxidised with chromic acid, yields cinchonic acid and a substance (not yet investigated) resembling meroquininine (Koenigs, Abstr., 1894, i, 392).

The following new compounds and properties are described: *α*-isocinchonine dissolves in 70 parts of light petroleum, the hydrochloride crystallises with $3H_2O$ (not $2H_2O$ as previously described, *loc. cit.*), and the acid sulphate crystallises with $3\frac{1}{2}H_2O$ in needles; hydriodo-cinchonine dissolves in 57 parts of absolute alcohol, and its dihydriodide in about 11 parts of 50 per cent. alcohol; *allocinchonine* sulphate dissolves in 120 parts of water at 21° ; cinchonine chloride crystallises with $2H_2O$, melts at 82° , but when anhydrous at 72° , and has a specific rotation $[\alpha]_D + 48.77^\circ$; its *hydrochloride*, $C_{19}H_{21}N_2Cl, HCl$, crystallises in white, matted needles, which melt at 213 — 214° ; cinchonine dissolves in 70 parts of toluene, in 150 parts of a mixture of equal parts of toluene and chloroform, and in 200 parts of a similar mixture of benzene and chloroform; *cinchoninephenylurethane* crystallises in tablets and melts at 198° ; *α*-isocinchoninephenylhydrazone melts and decomposes at 108 — 109° ; *α*-iso-*ψ*-cinchonine hydriodide, $C_{19}H_{22}ON_2, HI, H_2O$, crystallises in prismatic tables, and when anhydrous melts at 235 — 236° ; the *oxalate*, $(C_{19}H_{22}ON_2)_2, H_2C_2O_4, 6H_2O$, crystallises in flakes.

R. H. P.

Oxidation Products of Cotarnine. By G. F. WULFF (*Bull. Acad. St. Petersb.*, 1899, [v], 11, 45—57).—When cotarnine is oxidised in alkaline solution with potassium permanganate, the principal products are oxycotarnine, cotarnmethylinine, and carbon dioxide, small quantities of potassium cotarnate and oxalate being also formed.

Oxycotarnine, $\text{CH}_2 \begin{array}{c} \diagup \text{O} \cdot \text{C} \text{---} \text{C} \text{---} \text{C} \text{---} \text{CO} \cdot \text{NMe} \\ \diagdown \text{O} \cdot \text{C} \cdot \text{C}(\text{OMe}) \cdot \text{CH} \cdot \text{C} \cdot \text{CH}_2 \cdot \text{CH}_2 \end{array}$, crystallises from water in colourless prisms containing $1\text{H}_2\text{O}$, and melting at $69\text{--}70^\circ$; at $50\text{--}90^\circ$, the water is expelled, the anhydrous compound obtained having a melting point of 108° . It is slightly soluble in light petroleum, more so in ether, and readily in alcohol, chloroform, benzene, or water; it is precipitated from its aqueous solution by strong potassium hydroxide solution, and is not changed on boiling with concentrated hydrochloric acid. It dissolves readily in concentrated sulphuric acid, and on warming the solution assumes a purple colour, whilst if the cooled liquid is mixed with a few drops of water, it becomes violet. It does not form an acetyl compound, but yields a *bromo-derivative*, $\text{C}_{12}\text{H}_{12}\text{O}_4\text{NBr}$, which is deposited as a white, crystalline precipitate, gradually changing to slender, silvery needles which are soluble in water and melt at $125\text{--}126^\circ$. The *aurichloride* forms a slightly soluble, yellow, crystalline precipitate, melting and decomposing at 160° , and the *platinichloride*, $(\text{C}_{12}\text{H}_{13}\text{O}_4\text{N})_2 \cdot \text{H}_2\text{PtCl}_6$, separates in rectangular, orange plates, which darken at 100° , and melt and decompose at $179\text{--}180^\circ$.

Cotarnmethylinine, $\text{CH}_2 \begin{array}{c} \diagup \text{O} \\ \diagdown \text{O} \end{array} \text{C}_6\text{H}(\text{OMe}) \begin{array}{c} \diagup \text{CO} \\ \diagdown \text{CO} \end{array} \text{NMe}$, crystallises from alcohol or a mixture of alcohol and chloroform in slender, white, fibrous needles, which sublime at $190\text{--}195^\circ$, and melt and decompose at $205\text{--}206^\circ$; it is only slightly soluble in water, but dissolves readily in concentrated sulphuric acid, forming a yellowish-orange liquid. When heated with potassium hydroxide solution, it yields methylinine and cotarnic acid. T. H. P.

Cytisine and its Alkyl Derivatives. By A. RAUWERDA (*Chem. Centr.*, 1900, ii, 268—269; from *Ned. Tijds. Pharm.*, 12, 161—173).—Cytisine distils at 218° under a pressure of 2 mm., forming a colourless liquid, which afterwards solidifies, and a sublimate consisting of slender needles. It separates from alcohol in rhombic crystals, and when treated with nitrobenzene containing dinitrothiophen it gives a rather stable, reddish-violet coloration; with coniine, it forms a similar, but much more evanescent, coloration. Data regarding the solubility of cytisine in chloroform, methyl alcohol, ethyl alcohol, benzene, acetone, and ethyl acetate at various temperatures are quoted. The rotatory power of cytisine in 15 per cent. aqueous solution at 12° is $[\alpha]_D -127.40'$, and this constant increases to a concentration of 20 per cent. and then again decreases. The original paper contains copious data in reference to the rotatory power in various solvents. *Methylcytisine*, prepared by heating cytisine with a slight excess of methyl iodide at 100° , crystallises from alcohol in long columns, and from water in plates. It is easily soluble in water, chloroform, methyl alcohol, ethyl alcohol, benzene, or acetone. The rotatory power in 10

per cent. aqueous solution is $[\alpha]_D - 234^{\circ}10'$, and attains a maximum at a concentration of about 25 per cent. *Ethylcystisine* was obtained only as a syrup. *Cetylcystisine* crystallises from alcohol in slender, white needles, melts at $55-56^{\circ}$, is readily soluble in alcohol, methyl alcohol, or chloroform, and insoluble in water; in 5 per cent. chloroform solution at 8° , the rotatory power is $[\alpha]_D - 112^{\circ}$. E. W. W.

Crystalline Form of Histidine Dichloride. By ARTHUR SCHWANTKE (*Zeit. physiol. Chem.*, 1900, 29, 493).—Histidine dichloride [orthorhombic, $a:b:c = 0.76537:1:1.77516$] is apparently isomorphous with histidine monochloride [$a:b:c = 0.76665:1:1.71104$]; since the latter contains $1H_2O$, whilst the former is anhydrous, the second mol. of hydrogen chloride in the dichloride appears to fulfil the same function as the water of crystallisation of the monochloride.

W. A. D.

Tetramethyldiaminodiphenylmethane and similar Substances. By GEORG COHN (*Chem. Zeit.*, 1900, 24, 564. Compare Abstr., 1895, i, 98).—Tetramethyldiaminodiphenylmethane is most readily obtained when 16 parts of dimethylaniline, 6 of formaldehyde solution (40 per cent.), and 20 of hydrochloric acid (25 per cent.) are heated for several hours on the water-bath. A smaller amount of acid may be employed or else zinc chloride. Diphenylmethane derivatives cannot be obtained from dimethyl-*o*-toluidine. Both diethylaniline and methyldiphenylamine, however, readily enter into condensation; in the latter case, the reaction is violent, and it is necessary to employ acetic in place of hydrochloric acid. The product is a yellowish-white powder insoluble in the ordinary solvents, and when oxidised with dichromate in the presence of acetic and hydrochloric acid yields blue or green dyes. J. J. S.

Direct Synthesis of Ketodihydroquinazolines from Ortho-amino-acids. By MARSTON TAYLOR BOGERT and AUGUST HENRY GOTTHELF (*J. Amer. Chem. Soc.*, 1900, 22, 522—535. Compare this vol., i, 412).—When anthranilic acid (1 mol.) and acetonitrile (2—3 mols.) are heated together in a sealed tube for 6 hours at $200-210^{\circ}$, 2-methyl-4 ketodihydroquinazoline is formed, identical with that obtained by Weddige (Abstr., 1885, 661; 1887, 1044), by Bischler and Burkart (Abstr., 1893, i, 530), and by Niementowski (Abstr., 1895, i, 571), carbon dioxide and acetanilide being also produced. The yield of the quinazoline is increased by the addition of acetic anhydride; neither acetic anhydride nor acetyl chloride react with it under ordinary conditions. The same compound also results from the action of acetonitrile on acetylanthranilic acid, and of acetic anhydride on acetylanthranilic nitrile.

The authors have repeated the method of preparation described by Niementowski (*loc. cit.*), and, in addition to 2-methyl-4-ketodihydroquinazoline, have obtained acetanilide, and a substance which crystallises in needles, melts at $194-195^{\circ}$, and yields the quinazoline when boiled with hydrochloric acid, or on sublimation.

A number of salts of the quinazoline were prepared and found to possess generally the characters ascribed to them by Niementowski

(Abstr., 1896, i, 578). The methyl ether melts at 72°, or, when anhydrous, at 111°, and is therefore identical with the $\beta\gamma$ -dimethyl- $\Delta\psi$ -oxyquinazoline of Weddige (Abstr., 1887, 1044).

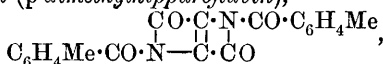
It has been stated by Bedson (Trans., 1880, 37, 756) that, by the action of acetic anhydride on anthranilic acid, diacetylanthranilic acid is formed; the present authors, however, could not obtain this compound, but only the monoacetyl derivative. E. G.

Constitution of Hippuroflavin. By LEOPOLD RÜGHEIMER (*Annalen*, 1900, 312, 81—90).—A discussion of the respective claims of the formulæ advocated by the author and by Erlenmeyer, jun.

M. O. F.

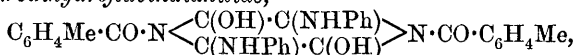
Homologues of Hippuroflavin. By LEOPOLD RÜGHEIMER and F. FEHLHABER (*Annalen*, 1900, 312, 65—80. Compare Abstr., 1896, i, 61).—*Ethyl p-tolurate*, $C_6H_4Me \cdot CO \cdot NH \cdot CH_2 \cdot CO_2Et$, dissolves very readily in alcohol, ether, benzene, or chloroform, but more sparingly in petroleum, from which it crystallises in long needles melting at 69°.

p-Toluroflavin (*p-dimethylhippuroflavin*),



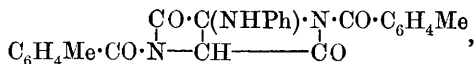
obtained by the action of phosphorus pentachloride on ethyl tolurate (compare Abstr., 1894, i, 55), is insoluble in ether, benzene, chloroform, or petroleum, and almost insoluble in alcohol; it crystallises from hot glacial acetic acid in aggregates of small, yellow needles, and becomes brown when heated, but does not melt at 285°.

p-Tolurodihydroflavindianilide,



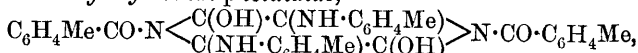
produced when *p*-toluroflavin is heated with aniline (2 mols.) and glacial acetic acid, is insoluble in common solvents; the solution in alcoholic potash is yellow.

p-Toluroflavinanilide,

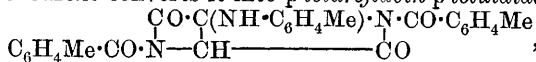


formed on heating tolurodihydroflavindianilide with nitrobenzene in a reflux apparatus during 30 minutes, crystallises from alcohol in small, yellow, silky needles, and melts at 255—257°, when it decomposes.

p-Tolurodihydroflavindi-p-toluidide,



prepared from *p*-toluroflavin and *p*-toluidine, does not melt at 270°; boiling nitrobenzene converts it into *p-toluroflavin-p-toluidide*,



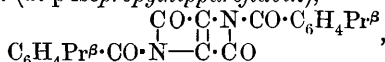
which crystallises from alcohol in small, golden, lustrous needles which remain unfused at 270°.

Ethyl o-tolurate, $C_6H_4Me \cdot CO \cdot NH \cdot CH_2 \cdot CO_2Et$, crystallises from water in needles and melts at 55°.

o-Toluroflavin (*o-dimethylhippuroflavin*), $C_{20}H_{14}O_4N_2$, crystallises from hot alcohol in small, yellow needles which darken when heated; it does not melt at 285°.

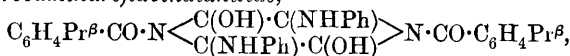
Ethyl cuminurate, $C_6H_4Pr^{\beta} \cdot CO \cdot NH \cdot CH_2 \cdot CO_2Et$, crystallises from ether in small needles and melts at 49° .

Cuminuroflavin (*di-p-isopropylhippuroflavin*),

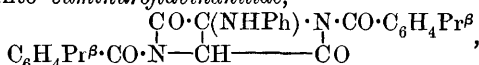


crystallises from alcohol and from acetic acid in thin plates with golden lustre and melts at $230-235^{\circ}$, when it decomposes.

Dihydrocuminuroflavindianilide,

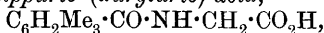


is very sparingly soluble in common solvents; boiling nitrobenzene converts it into *cuminuroflavinanilide*,



which crystallises from amyl alcohol in pale yellow, silky needles and does not melt at 290° .

2:4:5-Trimethylhippuric (*duryluric*) acid,



crystallises from water in large, lustrous plates or in stellate aggregates of needles and melts at 167° ; the *calcium*, *barium*, and *zinc* salts contain $3H_2O$, $4H_2O$, and $2\frac{1}{2}H_2O$ respectively. The *ethyl* ester crystallises in small needles and melts at 96° . M. O. F.

Derivation and Rational Nomenclature of the Quinopyridines. By CONRAD WILLGERODT (*Chem. Zeit.*, 1900, **24**, 437—439).—This paper consists of a discussion of the constitution and nomenclature of the 28 possible isomeric quinopyridines. E. G.

Formation of Safranines. By D. A. CHARDIN (*J. Russ. Phys. Chem. Soc.*, 1900, **32**, 309—324).—The formation of safranines by the oxidation of 1 mol. of a *p*-diamine with 2 mols. of a primary monoamine is influenced by the number and position of the methyl groups of the monoamine, and the author's experiments in this direction lead to the following conclusions. When the monoamine has only one methyl group in the molecule, the relative position of the methyl and amino-groups has no influence on the formation of safranines, which can thus be obtained with *o*-, *m*-, or *p*-toluidine. When two or more methyl groups are present in the molecule of the monoamine, for the formation of a safranine, it is necessary that one of them should be in the *p*-position to the amino-group, and that the others can be divided into pairs of groups in the *p*-position to one another; if the number of methyl groups be even, the remaining one may occupy any position.

The preparation of safranines by the oxidation of a monoamine in presence of nitrosodimethylaniline hydrochloride can be explained according to two different schemes of condensation, between which the facts are insufficient to admit of a decision being formed. T. H. P.

Reduction of Aromatic Aldazines. Synthesis of Benzylhydrazine. By THEODOR CURTIUS [in part with E. HAAGER, E. HARDING, A. PROPFE, and G. SPRENGER] (*J. pr. Chem.*, 1900, [ii], **62**, 83—126).—The substance prepared by Curtius and Quedenfeldt

(Abstr., 1899, i, 276) by reducing benzaldazine with sodium amalgam is *benzylbenzylidenehydrazine*, $\text{CH}_2\text{Ph}\cdot\text{NH}\cdot\text{N}:\text{CHPh}$, and not *dibenzylhydrazine*, as was previously supposed; the *hydrochloride*, *picrate*, *acetyl*, *benzoyl*, and *nitroso*-derivatives are also hydrazones, and the oxidation product is not 'bis-azidiphenylmethane,' but *dibenzylidibenzylidenehydrotetrazone*, $\text{N}_2(\text{CH}_2\text{Ph})_2(\text{N}:\text{CHPh})_2$. *s*-Dibenzylhydrazine is, however, also formed in the reduction: the *hydrochloride* forms glistening flakes, only slightly soluble in cold water, and melts at 225° ; the *base* crystallises from dilute alcohol, melts at about 47° , and readily decomposes; the *diacetyl* derivative crystallises from alcohol in prisms and melts at $117\text{--}118^\circ$; the *dibenzoyl* derivative crystallises from alcohol in minute needles and melts at 164° ; the *dinitroso*-derivative forms pale yellow crystals and melts at $35\text{--}40^\circ$; when crystallised from alcohol or heated at $30\text{--}40^\circ$, it evolves red fumes and is converted into the nitrosohydrazone referred to above. A small amount of benzylamine is also produced in the reduction of benzaldazine.

Benzylbenzylidenehydrazine is hydrolysed by hydrochloric acid to benzaldehyde and *benzylhydrazine*, $\text{CH}_2\text{Ph}\cdot\text{NH}\cdot\text{NH}_2$; the *hydrochloride* of the latter crystallises from alcohol in glistening flakes, dissolves very readily in water, and melts at 111° ; the *base* is a colourless oil, which boils at 135° under 29 mm. pressure, readily decomposes with loss of nitrogen, and condenses like phenylhydrazine with aldehydes, ketones, and ethyl acetoacetate.

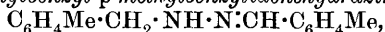
Benzyl-o-hydroxybenzylidenehydrazine, $\text{CH}_2\text{Ph}\cdot\text{NH}\cdot\text{N}:\text{CH}\cdot\text{C}_6\text{H}_4\cdot\text{OH}$, crystallises from dilute alcohol in pale yellow flakes and melts at 90° .

Pyruvic acid benzylhydrazone, $\text{CH}_2\text{Ph}\cdot\text{NH}\cdot\text{N}:\text{CMe}\cdot\text{CO}_2\text{H}$, crystallises from dilute alcohol in stout, white prisms and melts at 104° .

Benzylsemicarbazide, $\text{CH}_2\text{Ph}\cdot\text{NH}\cdot\text{NH}\cdot\text{CO}\cdot\text{NH}_2$, crystallises from dilute alcohol and melts at about 135° . *Phenylbenzylthiosemicarbazide*, $\text{CH}_2\text{Ph}\cdot\text{NH}\cdot\text{NH}\cdot\text{CS}\cdot\text{NHPh}$, crystallises from alcohol in flakes and melts at 116° . *Dibenzoylbenzylhydrazine*, $\text{CH}_2\text{Ph}\cdot\text{N}_2\cdot\text{HBz}_2$, crystallises from dilute alcohol in prisms and melts at 148° . Hydrochloric acid slowly hydrolyses benzylhydrazine to benzyl chloride and hydrazine.

By reduction with zinc dust and acetic acid, benzaldazine is converted into ammonia and dibenzylamine. *p*-Methylbenzaldazine is similarly reduced to *di-p-methylbenzylamine*, $\text{NH}(\text{CH}_2\cdot\text{C}_6\text{H}_4\text{Me})_2$; the *hydrochloride* crystallises from alcohol in glistening flakes and melts at 272° ; the *base* forms stout, tabular crystals, melts at 32.5° , and boils at $192\text{--}193^\circ$ under 13 mm. pressure; the *nitrate* forms white tablets, only slightly soluble in water, and melts at 213° ; the *picrate* crystallises from alcohol or light petroleum in stout, red tablets and melts at 153° ; the *platinichloride* forms pale yellow flakes and melts at 188° ; the *mercurichloride* separates from dilute alcohol in large crystals and melts at 112° ; the *nitrite* melts at 145° and can be crystallised from alcohol; it is, however, readily converted into the *nitroso*-derivative, which separates from alcohol in colourless needles and melts at 52° .

When reduced with sodium amalgam, *p*-methylbenzaldazine is converted into *p-methylbenzyl-p-methylbenzylidenehydrazine*,



which crystallises from alcohol in large tablets, melts at 101° , does not reduce Fehling's solution, and rapidly decomposes in the air; the *picrate* crystallises from alcohol in golden-yellow needles and melts at 132° ; the *acetyl* derivative crystallises from alcohol in thick flakes and melts at 95° ; the *benzoyl* derivative crystallises from alcohol in minute needles and melts at 130.5° ; the *nitroso*-derivative crystallises from alcohol in yellow needles, melts at 111° , gives Liebermann's reaction, and is decomposed by dilute hydrochloric acid with formation of *p*-tolylaldehyde. *Di-p-methylbenzyl-di-p-methylbenzylidenehydrotetrazone*, $N_2(CH_2 \cdot C_6H_4Me)_2(N \cdot CH \cdot C_6H_4Me)_2$, prepared by oxidising the hydrazine with mercuric oxide, crystallises from alcohol in minute needles and melts at 163° ; excess of the oxide gives *p*-methylbenzalazine; hydrochloric acid gives *p*-methylbenzalazine and *p*-tolaldehyde.

The hydrazine is further reduced by sodium amalgam to *s-di-p-methylbenzylhydrazine*, $N_2H_2(CH_2 \cdot C_6H_4Me)_2$; the *hydrochloride* is insoluble in cold water, crystallises from dilute alcohol in minute, glistening needles, and melts at 236° ; the *base* separates from ether in pale yellow crystals, melts at 67° , and rapidly decomposes; the *diacetyl* derivative crystallises from alcohol in minute, colourless needles and melts at 112° ; nitrous acid converts the hydrazine into the nitroso-derivative of the hydrazine; picric acid also yields the picrate of the hydrazine; mercuric oxide oxidises it directly to methylbenzalazine.

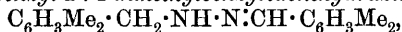
p-Methylbenzylhydrazine hydrochloride, $C_6H_4Me \cdot CH_2 \cdot NH \cdot NH_2 \cdot HCl$, prepared by hydrolysing the hydrazine with hydrochloric acid, crystallises from alcohol in glistening plates and melts at 152° ; the *base* boils at 135° under 18 mm. pressure, solidifies to a crystalline mass which melts at $40-41^{\circ}$, and reduces Fehling's solution and ammoniacal silver solutions in the cold; the *picrate* crystallises from water in yellow needles and melts with decomposition at 144° . *p-Methylbenzyl-o-hydroxybenzylidenehydrazine*, $OH \cdot C_6H_4 \cdot CH \cdot N \cdot NH \cdot CH_2 \cdot C_6H_4Me$, crystallises from alcohol in pale yellow, glistening flakes and melts at 105° . *p-Methoxybenzyl-p-methylbenzylidenehydrazine* crystallises from dilute alcohol in microscopic needles and melts at 88° . *Pyruvic acid p-methylbenzylhydrazine*, $CO_2H \cdot CMe \cdot N_2H \cdot CH_2 \cdot C_6H_4Me$, crystallises from alcohol in glistening plates and melts at $77-78^{\circ}$. *p-Methylbenzylsemicarbazide*, $C_6H_4Me \cdot CH_2 \cdot NH \cdot NH \cdot CO \cdot NH_2$, crystallises from dilute alcohol in white flakes and melts at about 142° . *p-Methylbenzyl-phenylthiosemicarbazide* crystallises from dilute alcohol in large, glistening flakes and melts at $132-133$.

1-p-Methylbenzyl-3-methyl-5-pyrazolone, $C_6H_4Me \cdot CH_2 \cdot N \begin{smallmatrix} \diagup N=CMe \\ \diagdown CO \cdot CH_2 \end{smallmatrix}$, melts at $154-155^{\circ}$. *Di-benzoyl-p-methylbenzylhydrazine*, $C_6H_4Me \cdot CH_2 \cdot N_2HBz_2$, crystallises from alcohol in needles and melts at 165° . *p-Methylbenzylhydrazine* is hydrolysed by hydrochloric acid to hydrazine hydrochloride and *p*-methylbenzyl chloride, and the latter was characterised by converting it by Gabriel's method (Abstr., 1887, 1037) into *p-methylbenzyl-phthalimide*, which crystallises from dilute alcohol in long, white needles and melts at $116-117^{\circ}$.

2:4-Dimethylbenzalazine, $N_2(CH \cdot C_6H_3Me_2)_2$, separates from alcohol in stout crystals and melts at 118° ; the *hydrochloride* crystallises from

alcohol in small, glistening, yellow needles and melts at 178—179° with evolution of gas. It is reduced by zinc dust and acetic acid to 2:4-dimethylbenzylamine (Hinrichsen, Abstr., 1889, 131) and *di*-2:4-dimethylbenzylamine, $\text{NH}(\text{CH}_2 \cdot \text{C}_6\text{H}_3\text{Me}_2)_2$, which boils at 217—218° under 14 mm. pressure, and solidifies at 28.5°; the *hydrochloride* crystallises from water in colourless needles and melts at 226—227°; the *nitrate* forms large, white tablets, melts with decomposition at 211°, and is only very slightly soluble in hot water; the *picrate* crystallises from alcohol in indistinct, sulphur-yellow crystals and melts at 142—143°; the *platinichloride* separates from alcohol in red-brown crystals and melts with decomposition at 188°; the *mercurichloride* separates from alcohol in well-formed crystals and melts at 157°; the *nitrite* crystallises from alcohol in small, colourless needles, melts at 147°, and is converted, by evaporating with alcohol, into *nitrosodi*-2:4-dimethylbenzylamine, which separates from alcohol in small, pale yellow crystals and melts at 73°.

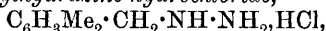
2:4-Dimethylbenzyl-2:4-dimethylbenzylidenehydrazine,



prepared by reducing the aldazine with sodium amalgam, crystallises from alcohol in glistening needles, melts at 77—78°, and decomposes rapidly; the *picrate* crystallises from alcohol in bunches of yellow needles and melts at 127—128°; the *acetyl* derivative crystallises from alcohol in long, hair-like needles and melts at 137.5°; the *benzoyl* derivative crystallises from alcohol in felted needles and melts at 136°; the *nitroso*-derivative crystallises from alcohol in bundles of long, yellow needles and melts at 68°. *Di*-2:4-dimethylbenzyl*di*-2:4-dimethylbenzylidenehydrotetrazone, $\text{N}_2(\text{CH}_2 \cdot \text{C}_6\text{H}_3\text{Me}_2)_2(\text{N} \cdot \text{CH} \cdot \text{C}_6\text{H}_3\text{Me}_2)_2$, separates from alcohol in pale yellowish granules and melts at 137—138° with evolution of gas.

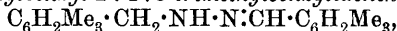
s-*Di*-2:4-dimethylbenzylhydrazine, $\text{N}_2\text{H}_2(\text{CH}_2 \cdot \text{C}_6\text{H}_3\text{Me}_2)_2$, prepared by further reduction of the hydrazone with sodium amalgam, crystallises from alcohol in long, white needles, melts at 58.5°, and gradually decomposes in the air; the *hydrochloride* crystallises from alcohol in glistening, white needles, melts at 200°, and is almost insoluble in boiling water; the *diacetyl* derivative crystallises from alcohol in colourless flakes and melts at 125°; nitrous acid converts the hydrazine into the nitroso-derivative of the hydrazone; mercuric oxide oxidises it to the tetrazone and the aldazine.

2:4-Dimethylbenzylhydrazine hydrochloride,



crystallises from alcohol in long, glistening needles, melts at 170—171°, and reduces ammoniacal silver and Fehling's solutions in the cold. 2:4-Dimethylbenzylbenzylidenehydrazine, $\text{C}_6\text{H}_3\text{Me}_2 \cdot \text{CH}_2 \cdot \text{NH} \cdot \text{N} \cdot \text{CHPh}$, crystallises from alcohol in short, stout needles, melts at 92—93°, and is fairly stable in the air.

2:4:5-Trimethylbenzyl-2:4:5-trimethylbenzylidenehydrazine,



crystallises from alcohol in unstable, silky needles and melts at 134°; the *picrate* crystallises from ether in yellow needles and melts at 169°; the *acetyl* derivative crystallises from alcohol in long, slender needles and melts at 184°; the *benzoyl* derivative crystallises from alcohol in

long needles and melts at 187° , and the *nitroso*-derivative melts at 118° .

s-Di-2:4:5-trimethylbenzylhydrazine, $\text{N}_2\text{H}_2(\text{CH}_2\cdot\text{C}_6\text{H}_2\text{Me}_3)_2$, crystallises from alcohol in unstable, rhombic crystals and melts at 128° ; the *hydrochloride* crystallises from alcohol in long, hair-like needles, melts at $170\text{--}171^{\circ}$, and is only slightly soluble in water; nitrous and picric acids yield derivatives of the hydrazone.

2:4:5-Trimethylbenzylhydrazine, $\text{C}_6\text{H}_2\text{Me}_3\cdot\text{CH}_2\cdot\text{NH}\cdot\text{NH}_2$, solidifies to a mass of white crystals and rapidly decomposes with loss of nitrogen; the *hydrochloride* crystallises from water or alcohol in needles and melts at $239\text{--}240^{\circ}$; the *picrate* crystallises from alcohol in yellow, monoclinic needles and begins to decompose at 163° . *2:4:5-Trimethylbenzylbenzylidenehydrazine*, $\text{C}_6\text{H}_2\text{Me}_3\cdot\text{CH}_2\cdot\text{NH}\cdot\text{N}:\text{CHPh}$, crystallises from alcohol in unstable tablets and melts at $89\text{--}90^{\circ}$. *2:4:5-Trimethylbenzylsemicarbazide*, $\text{C}_6\text{H}_2\text{Me}_3\cdot\text{CH}_2\cdot\text{NH}\cdot\text{NH}\cdot\text{CO}\cdot\text{NH}_2$, crystallises from water in white needles and melts at $174\text{--}175^{\circ}$. *Phenyl-2:4:5-trimethylbenzylthiosemicarbazide*, $\text{C}_6\text{H}_2\text{Me}_3\cdot\text{CH}_2\cdot\text{NH}\cdot\text{NH}\cdot\text{CS}\cdot\text{NPh}$, crystallises from alcohol in silky needles and melts at $167\text{--}168^{\circ}$. *Pyruvic acid 2:4:5-trimethylbenzylhydrazone*, $\text{C}_6\text{H}_2\text{Me}_3\cdot\text{CH}_2\cdot\text{NH}\cdot\text{N}:\text{CMe}\cdot\text{CO}_2\text{H}$, crystallises from alcohol in silky needles and melts at $91\text{--}92^{\circ}$. T. M. L.

Combination of Magenta with the Sulpho-conjugated Azo-colouring Matters. By ALPHONSE SEYEWETZ (*Compt. rend.*, 1900, 131, 472—474).—Naphthylamine-brown, crystallised ponceau, and solid red D, which contain respectively 1, 2, and 3 sulphonic groups neutralised by an alkali, combine respectively with 1, 2, and 3 mols. of magenta. In presence of an excess of alkali, however, naphthylamine-brown will combine with 2 mols. of magenta; it is the only one of the three that contains a hydroxyl group in a nucleus in which the sulphonic group has not been substituted.

Tropæolin V, chrysoin, Orange I and Orange II, which contain one sulphonic group and various hydroxyl groups, each combine with 1 mol. of magenta when the sulphonic group only is neutralised, but in presence of excess of alkali, they each combine with 2 mols. of magenta. In all of them there is at least one hydroxyl group in a nucleus in which the sulphonic group has not been introduced.

Crystallised ponceau, chromotrope 2R, chrome-brown RR, solid yellow A, jaune soleil, brilliant crocein M, Congo-red, and diamine-black BO all contain two sulphonic groups, together with various substituted radicles, and all combine with 2 mols. of magenta, but chrome-brown RR, which is the only one containing a hydroxyl group in a nucleus that does not contain a sulphonic group, combines with 3 mols. of magenta in presence of sufficient alkali to neutralise the hydroxyl group.

Ponceau 5R and diamine-blue combine with as many mols. of magenta as they contain sulphonic groups neutralised by an alkali, but benzo-orange R combines with 2 mols. magenta, probably owing to the presence of a carboxyl group. It contains a hydroxyl group in a nucleus which does not also contain a sulphonic group, and consequently in presence of excess of alkali it combines with a third mol. of magenta. C. H. B.

Isomeric Forms of Diazoaminobenzenedi-*p*-sulphonic Acid. By WILHELM VAUBEL (*Zeit. angew. Chem.*, 1900, 31, 762—763).—Whereas the diazoamino-compound prepared from sodium sulph-anilate at 0° is sparingly soluble in water and crystallises in slender, yellow needles, that obtained at 10—14° is easily soluble and is only precipitated by saturating the solution with common salt and adding a large quantity of glacial acetic acid. The yellowish-brown powder thus obtained is contaminated with sodium chloride and sodium acetate, but a determination of the ratio of sulphur to nitrogen shows it to have the same composition as the product obtained at 0°. Moreover, the latter on heating at 100° yields the corresponding amino-azo-compound, yet the soluble modification remains unchanged. It is suggested that the sparingly soluble modification probably has the formula $\text{SO}_3\text{H}\cdot\text{C}_6\text{H}_4\cdot\text{N}:\text{N}\cdot\text{NH}\cdot\text{C}_6\text{H}_4\cdot\text{SO}_3\text{H}$, and the soluble modification either the formula $\text{SO}_3\text{H}\cdot\text{C}_6\text{H}_4\cdot\text{N}:\text{N} > \text{NH}$ or $\text{NH}(\text{N}\cdot\text{C}_6\text{H}_4\cdot\text{SO}_3\text{H})_2$.

W. A. D.

Influence of Nitrogenous Substances on the Heat-coagulation of Proteids. By KARL SPIRO (*Zeit. physiol. Chem.*, 1900, 30, 182—199).—The observations were made on various proteids, but mostly on egg-albumin. Increase in the concentration of the solution lowers the coagulating point somewhat. It is necessary to take this factor and also the rate of heating into account. Choline, as Mauthner (*Med. Jahrbücher*, 1874, 347) originally stated, lowers the coagulation point, and ultimately prevents coagulation; and its solutions will even dissolve fibrin and coagulated albumin. Other basic substances, such as piperidine, pyridine, aniline, and xylydine, act similarly. Beyond a certain point, pyridine and urethane precipitate proteid in the cold. Formamide in small quantities raises the coagulating point; increase in its amount depresses it; finally, there is precipitation in the cold, but on heating, the proteid remains in solution. Urea in small amount raises the coagulation point considerably, but with greater concentration prevents coagulation entirely. Considerable importance is attached to these experiments with urea, on account of the occurrence of proteids in urine. The action of urea resembles that of alkalis, and a substance analogous to alkali-albumin is believed to be formed.

W. D. H.

Bence-Jones Albumin. By ADOLF MAGNUS-LEVY (*Zeit. physiol. Chem.*, 1900, 30, 200—240).—A case of Bence-Jones albumin occurring in the urine is described, and the characters of this remarkable proteid are examined in full. The case was one of bone disease, apparently similar to those in which the condition has been previously described. A review of the previous cases described leads to the conclusion that the same proteid occurred in all. The most noteworthy difference of opinion here expressed between the present author and those who preceded him is that the proteid is not an albumose, but an albumin, on the ground of elementary analysis and its reactions. Under certain conditions, it is completely coagulated by heat; here Spiro's observations (see preceding abstract) are duly taken into account. On digestion with gastric juice, it yields the usual series of

digestive products, with the exception of hetero-albumose. By slow concentration of a solution in ammonium sulphate, the proteid was obtained in a crystalline form.

It is believed to originate, not from the small bony tumours, but from the liver. The same opinion was expressed by Noël Paton respecting his crystalline globulin. How the bone disease affects the metabolism in the liver so as to lead to the discharge of this proteid remains an open question.

W. D. H.

Proteids of the Egg Yolk. By THOMAS BURR OSBORNE and GEORGE F. CAMPBELL (*J. Amer. Chem. Soc.*, 1900, 22, 413—422).—Sodium chloride solutions dissolve from egg yolk a large amount of substance which is precipitated on diluting or dialysing the solution. This globulin contains 15—30 per cent. of lecithin, and of the fractions that are obtained by fractional precipitation, those which are the more soluble contain the more lecithin; these compounds might well be called *lecithin-nucleovitellin*. The lecithin is removed readily by alcohol, but not by ether.

The insoluble proteid free from lecithin, *nucleovitellin*, has a constant composition when prepared from different fractions of the lecithin compound; when digested with pepsin, it yields paranuclein of varying composition. If all the phosphorus in these two substances is assumed to be present as H_3PO_4 or $H_8P_2O_9$ (or some very simple organo-phosphoric acid), and the amounts of hydrogen, oxygen, and phosphorus in this are subtracted from those found in the original substances, the composition of the remainder is the same whether the substance under consideration is the paranuclein or the paranucleo-proteid from which it is derived. Probably, therefore, both substances are compounds, in different proportions, of the same proteid, *vitellin*, with some derivative of phosphoric acid. The composition of the two substances named is:

	C.	H.	O (diff.).	N.	S.	P.
Nucleovitellin...	51.24	7.16	23.24	16.38	1.04	0.94
Vitellin	52.71	7.46	22.14	16.64	1.05	—

C. F. B.

Influence of Phosphates and other Inorganic Compounds on the Proteolytic Diastase of Malt. By AUG. FERNBACH and L. HUBERT (*Compt. rend.*, 1900, 131, 293—295. Compare this vol., i, 576).—The activity of the proteolytic diastase of malt is greatly increased by the addition of acid just up to the point at which the alkalinity to methyl-orange is neutralised, but if this limit is exceeded in the smallest degree the activity of the diastase is markedly reduced. Alkali phosphates have a retarding effect due to their alkalinity. Salts of calcium, magnesium, and aluminium, which precipitate part of the phosphates, accelerate the action of the diastase, but when added in excess may exert a distinctly retarding action. The different results obtained with diastases partially purified by precipitation with alcohol, &c., are probably due to the more or less complete removal of some of the phosphates.

C. H. B.

Organic Chemistry.

Composition of Roumanian Petroleum. By PETRU PONI (*Chem. Centr.*, 1900, ii, 452; from *Anal. Acad. romane*, 23).—The composition of petroleum from Colibasi has been determined by fractionally distilling from 0—100°. The petroleum does not contain acetylene or ethylene hydrocarbons, but in the fraction boiling below 10° small quantities of ethane, propane, butane, *n*-pentane, and *tert*.pentane were found. From the portion boiling at 26—36°, *isopentane* was isolated; this, when oxidised by fuming nitric acid, forms carbon dioxide, acetic acid, and two solid substances which have not yet been examined. The fraction distilling at 50—52° has a maximum sp. gr. 0.6963 at 0°/0°, and, therefore, probably contains *cyclopentane* and *tert*.hexane. Several isomeric hexanes also appeared to be present in the fraction boiling at 58—70°. The portion boiling at 64—66° to 74—76° contained small quantities of benzene which passed over with the hexane and methyl*cyclopentane* vapours. Methyl*cyclopentane* boils at 70—72°, and, on oxidation by fuming nitric acid, not only yields carbon dioxide and acetic acid, but also oxalic, succinic, and glutaric acids. The fraction boiling at 80—82° has a sp. gr. 0.7664 at 0°/0°, and contained *cyclohexane*, whilst that at 90—100° consisted largely of heptane mixed with toluene. The fraction obtained at 90—92° showed a minimum sp. gr. These fractions probably also contained methyl*cyclohexane* which boils at 102°, for after removing toluene and rectifying eight times, the sp. gr. was still 0.7345—0.7515. E. W. W.

Decomposition of Viscous Substances (Lubricating Oils) by Distillation under Pressure. By GUSTAV KRAEMER and ADOLF SPILKER (*Ber.*, 1900, 33, 2265—2270).—When phenylxylylethane, boiling at 270—310°, obtained from crude xylene by treatment with sulphuric acid, is distilled under a pressure of 10 atmospheres, methylanthracene, anthracene, toluene, and *ψ*-cumene are produced, together with a gas consisting chiefly of hydrogen and methane. Dicumyldimethylmethane behaves similarly when distilled under pressure, yielding dimethylantracene, tetramethylbenzene, xylene, and toluene.

When resin oil, 90 per cent. of which boils at 330—355° and has the composition $C_{18}H_{28}$, is distilled under a pressure of 25 atmospheres, phenanthrene, methylphenanthrene, cymene, methylcymene, and hydrocarbons richer in hydrogen are obtained, together with methane, hydrogen, and small quantities of olefines.

If 'bakunin' (lubricating oil prepared from Baku naphtha), boiling at 360—420°, is distilled under 25 atmospheres pressure, the products consist of naphthalene, paraffins, a considerable quantity of olefines, and a gas composed of methane and unsaturated hydrocarbons.

The authors conclude that the lubricating oils are not composed of polymeric olefines, but consist of cyclic compounds formed by the condensation of two or more molecules of hydrocarbons of the olefine or acetylene series. E. G.

Products of the Explosion of Acetylene and of Mixtures of Acetylene and Nitrogen. By WILLIAM G. MIXTER (*Amer. J. Sci.*, 1900, [iv], 10, 299—309. Compare this vol., i, 197).—The amounts of acetylene and hydrogen cyanide left after exploding mixtures of acetylene and nitrogen have been determined under a large variety of conditions. As a rule these amounts tend to increase as the proportion of nitrogen in the mixture increases, but the results are not regular; ammonia was detected in some cases, but not cyanogen. No hydrogen cyanide was formed when the gas was exploded in an iron U-tube cooled with water, but mixtures of acetylene and ammonia gave hydrogen cyanide when the gas was merely fired in an open jar at a comparatively low temperature. The relationship between the initial pressure and the amount of acetylene found after explosion has not been fully determined, but the quantity of acetylene increases up to 4 per cent. at 3 atmospheres pressure, and diminishes again at 5 atmospheres; the rapid cooling on exploding the gas in an iron U-tube causes no increase in the amount of acetylene, thus confirming the view that the acetylene found after the explosion is not an undecomposed residue, but is produced by a partial recombination of carbon and hydrogen.

T. M. L.

History of the Isonitro-compounds. By ARTHUR HANTZSCH (*Ber.*, 1900, 33, 2542—2543).—A controversial paper and claim for priority.

W. A. D.

Compounds of Ethylene and Allyl Alcohol with Mercuric Salts. By KARL A. HOFMANN and JULIUS SAND (*Ber.*, 1900, 33, 2692—2700).—The authors have confirmed experimentally all the facts dealt with in their former papers (this vol., i, 384 and 386) which have been called into question by Biilmann (this vol., i, 431). Ethyl ether mercury bromide, which Biilmann failed to obtain, dissolves in 6595 parts of absolute alcohol at 24°. Whereas ethanol mercury salts in alkaline solution yield no precipitate with potassium iodide, and a white precipitate, soluble in hot alkalis, with potassium sulphide, the ethyl ether mercury salts give rise in the first case to a white precipitate which changes to the iodide ($C_2H_3I(Hg)_n$) on heating, and in the second, to a white precipitate insoluble in hot alkalis. Moreover, the halogen-free, alkaline solution of an ether salt, unlike that of an ethanol salt, gives an insoluble carbonate when saturated with carbon dioxide. Biilmann's supposed ethanol mercuric sulphate is shown to have the composition $C_6H_{10}O_{12}S_2Hg_4$. Details are given for preparing the allene compounds of which Biilmann doubted the existence; since allenemercurey nitrate, $C_3H_3 \cdot HgNO_3$, is much more stable towards acids and oxidising agents (potassium permanganate and iodine) than allyl oxide mercuric nitrate, it appears probable that it is a mesitylene derivative, $(C_3H_3 \cdot HgNO_3)_3$, formed by polymerisation.

Under special conditions allyl alcohol interacts with mercuric salts in alkaline solution to yield *propylene glycol mercuric salts* of the type $C_3H_7O_2 \cdot HgX$, which differ strikingly from the allene and allyl oxide salts previously described. *Propylene glycol mercuric bromide*, $C_3H_7O_2 \cdot HgBr$, melts at 84—86°, decomposes at 110°, is easily soluble in alcohol and acetone, and is rapidly decomposed by hydrochloric acid; the alkaline

solution gives no precipitate with potassium iodide or cyanide or with hydrogen sulphide. Propenolmercuric bromide, on the other hand, melts at 251° , is insoluble in organic solvents, and is not attacked by dilute hydrochloric acid; with potassium iodide or cyanide or with hydrogen sulphide, the alkaline solution yields a white, insoluble iodide, cyanide, or sulphide. The glycol iodide, $C_3H_7O_2 \cdot HgI$, melts at about 80° , and closely resembles the bromide; it is decomposed by acetic acid with separation of mercuric iodide. Propenolmercuric iodide melts at 271° , and is not changed by 20 per cent. hydrochloric acid at the ordinary temperature.

W. A. D.

Some New Derivatives belonging to the Sugar Group. By WILLIAM ALBERDA VAN EKENSTEIN and CORNELIS A. LOBBY DE BRUYN (*Rec. Trav. Chim.*, 1900, 19, 178—182).—*Tribenzylidene-d-sorbitol*, obtained by the condensation of sorbitol with benzaldehyde in presence of hydrochloric acid, melts at 185° and has a rotatory power $[\alpha]_D + 30^{\circ}$ in 0.4 per cent. chloroform solution. *d*-Mannitol condenses with *o*-, *m*-, and *p*-nitrobenzaldehyde to form crystalline compounds which melt at 214° , 247° , and 162° respectively and have rotatory powers $[\alpha]_D - 59^{\circ}$, -30° , and -16° in 0.4 per cent. chloroform solution. *d*-Sorbitol reacts with *p*-nitrobenzaldehyde to form a compound which melts at 150° and has a rotatory power $[\alpha]_D - 58^{\circ}$. Experiments with dulcitol yielded negative results. *l*-Gulonic acid yields a monobenzaldehyde derivative which forms crystalline sodium and potassium salts, melts at 174° , and has a rotatory power $[\alpha]_D - 67^{\circ}$ in 1 per cent. methyl alcoholic solution. *l*-Idosaccharic acid reacts with 2 mols. of benzaldehyde to form a compound which melts at 211° and has a rotatory power $[\alpha]_D - 27^{\circ}$ in 0.4 per cent. methyl alcoholic solution; the sodium and potassium salts are syrupy. In the compounds formed by the condensation of *d*- and *l*-iditol with formaldehyde, three mols. of the latter are concerned, and not two as formerly stated. *i*-Trihydroxyglutaric acid (xylotrihydroxyglutaric acid) reacts with 1 mol. of formaldehyde to form a well crystallised compound which melts at 242° and is inactive. *l*-Gulonic acid reacts with two mols. of formaldehyde to form a compound which melts at 177° and has a rotatory power $[\alpha]_D - 88^{\circ}$ in 1 per cent. alcoholic solution. *l*-Idonic acid yields a similar compound which melts at 226° and has a rotatory power $[\alpha]_D - 54^{\circ}$ in 0.4 per cent. methyl alcoholic solution. *l*-Gulose forms a crystalline, yellowish *phenylbenzylhydrazone* which melts at 124° and has a rotatory power $[\alpha]_D - 24^{\circ}$ in 0.5 per cent. methyl alcoholic solution.

N. L.

Dimethyl Sulphate as an Alkylating Agent. By FRITZ ULLMANN and P. WENNER (*Ber.*, 1900, 33, 2476—2477).—Dimethyl sulphate can replace methyl iodide in all cases, and in general acts more rapidly and better; as it boils at 188° , open vessels may be used and the necessity for sealed tubes obviated. Aniline (2 mols.) with dimethyl sulphate (1 mol.) forms methylaniline and aniline methyl sulphate; *m*-nitraniline is converted into *m*-nitrodimethylaniline. Phenols can be methylated in a manner similar to the Schotten-Baumann method of benzoylation. The sodium salts of aromatic sulphonc acids are converted into methyl salts. Quinolines are con-

verted into quinolinium compounds, "aminonaphthacridines," phenyl-acridines, diaminoacridines, &c., into acridinium compounds, and aminophenazines into phenazonium compounds. Only the ring nitrogen is methylated in the latter cases; the amino-groups are not attacked, probably because the insoluble methyl-sulphate is precipitated before there has been time for a further action of the dimethyl sulphate to take place. C. F. B.

Decomposition of Alkyl Nitrates and Nitroglycerol by Alkalis, and the Relative Stability of Explosives. By MARCELLIN P. E. BERTHELOT (*Compt. rend.*, 1900, 131, 519—521).—When potassium hydroxide acts on nitroglycerol even in dilute solution, some potassium nitrite is formed, and hence it would seem that either some glyceraldehyde is produced during the reaction, which would then be analogous to the action of the alkali on ethyl nitrate, or the formation of aldehyde, and partial reduction of the nitric acid take place during the first action of the latter on the glycerol. In the latter case, the product, instead of being pure nitroglycerol, will be a nitroso-nitro-compound, and the presence of the nitrous acid derivative may exert an important influence on the stability of the compound. The presence of the nitroso-compound would not be detected by the ordinary method of analysis. C. H. B.

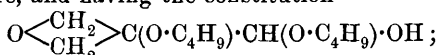
Reaction of Nitrous Esters with Alcohols and Ketones in Presence of Excess of Hydrogen Chloride [in Alcoholic Solutions]. By J. KISSEL (*J. Russ. Phys. Chem. Soc.*, 1900, 32, 390—419).—By the action of hydrogen chloride and ethyl alcohol on isoamyl nitrite, an ether of the composition $C_{15}H_{30}O_3$ is obtained (*J. Russ. Phys. Chem. Soc.*, 1896, 28, 882), and on heating with hydriodic acid in sealed tubes, this yields isoamyl iodide and a small proportion of ethyl iodide; the presence of the latter shows that the ethyl alcohol takes part in the formation of the ether.

When isoamyl nitrite, isoamyl alcohol, and hydrogen chloride react together, a colourless, oily compound, $C_{10}H_{22}O_3$, is obtained, which is volatile in a current of steam, boils at $170-173^\circ$, and is probably the isoamyl ether of ethylene glycol; it could not be obtained quite free from chlorine. On oxidation with alkaline permanganate, it yields (1) *α-ethoxy-γ-amylisovaleric acid*, $C_5H_{11} \cdot O \cdot CMe_2 \cdot CH(OEt) \cdot CO_2H$, a faint yellow, viscous liquid, slightly soluble in water, but readily so in aqueous ammonia or caustic alkalis, of which the silver and calcium salts were prepared; (2) oxalic acid, and (3) another acid, not yet identified, the silver salt of which forms pale yellow, granular crystals, and contains 38.41 per cent. of metal. If the oxidation is carried further, the last-named acid is found among the products, together with isovaleric acid and an ether-like substance boiling at $123-125^\circ$ under 40 mm. pressure.

In the reaction yielding the ether, $C_{15}H_{30}O_3$, various nitrogenous compounds are formed which are soluble in sodium hydroxide solution, and on adding a solution of a copper or mercury salt to the alkaline liquid a precipitate is at first formed, but afterwards dissolves; the action of hydrogen sulphide precipitates the metal, and yields a

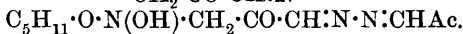
compound, $C_{10}H_{19}O_3N$, to which is ascribed the constitution $O-CH \cdot C_2H_4 \cdot O \cdot CH_2$
 $\begin{array}{c} | \qquad \qquad \qquad >CH_2 \qquad \qquad | \\ CH_2 \cdot N \cdot O \cdot C_2H_4 \cdot CHMe \end{array}$; it is a thick, brown syrup, which has a faint narcotic smell, is almost insoluble in water, and is not acted on by acids or alkalis, whilst with concentrated hydriodic acid it yields a basic compound.

The action of alcoholic hydrochloric acid on *isobutyl* nitrite in presence of alcohol gives rise to four compounds: (1) a *liquid* boiling at $175-178^\circ$ under 18 mm. pressure, and having the constitution $C_4H_9 \cdot O \cdot CMe_2 \cdot CH(OEt) \cdot OH$; (2) a *liquid* boiling at $180-188^\circ$ under 18 mm. pressure, and having the constitution

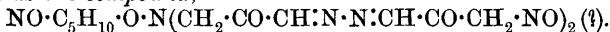


(3) oxalic acid, and (4) a brown, syrupy *acid* yielding a *calcium* salt, which, on analysis, gives results agreeing with those required for the formula $(C_4H_9 \cdot O \cdot CMe_2 \cdot CO_2)_2Ca$. Oxidation of compound (1) by means of an alkaline solution of potassium permanganate gives an *acid*, the silver salt of which has the composition $C_{10}H_{19}O_4Ag$ or $C_{10}H_{19}O_5Ag$.

The action of alcoholic hydrogen chloride on a mixture of acetone and *isoamyl* nitrite in molecular proportion yields (1) *isoamyloxyacetone*, $COMe \cdot CH_2 \cdot O \cdot C_5H_{11}$, which is a colourless liquid with a pleasant smell, and boils at $140-142^\circ$ under 25 mm. pressure. With phenylhydrazine, it gives the *compound* $N_2HPh(CMe \cdot CH \cdot NH \cdot NHPh)_2$, which separates from alcohol in pale yellow plates, darkens in the air, and melts at 147° ; on adding a little of this substance to concentrated sulphuric acid, a dirty-green coloration is formed, changing to yellow; (2) *s-diisoamyloxyacetone*, $CO(CH_2 \cdot OC_5H_{11})_2$; (3) a hard, brown, hygroscopic *resin*, having a faint narcotic smell and the probable constitution $C_5H_{11} \cdot O \cdot N \begin{array}{c} \diagup CH_2 \cdot CO \cdot CH \cdot N \\ \diagdown CH_2 \cdot CO \cdot CH \cdot N \end{array} O$, or



It gives a *mercury* salt, $C_{11}H_{19}O_4N_3 \cdot HgCl_2 \cdot 2HgCl$, and with nitrous acid yields the *compound*,



The products of the interaction of methyl propyl ketone, *isoamyl* nitrite, and hydrochloric acid in alcoholic solution are (1) the *compound*, $OH \cdot CH_2 \cdot CO \cdot [CH_2]_2 \cdot CH \cdot N \cdot O \cdot C_5H_{11}$, boiling at $165-170^\circ$ under 15 mm. pressure; (2) a *compound*, $C_{15}H_{25}ON_3$, which boils at $204-214^\circ$, under 25 mm. pressure, and gives with mercuric chloride a white, amorphous precipitate of the composition $C_{15}H_{25}ON_3 \cdot HgCl_2 \cdot HgCl$; (3) an amorphous, brown, hygroscopic *compound*, $C_{20}H_{33}O_9N_5$, which has a slightly narcotic odour, and forms a *mercury* derivative, $C_{20}H_{33}O_9N_5 \cdot HgCl_2 \cdot 2HgCl$.
T. H. P.

Preparation of Lecithin. By PETER BERGELL (*Ber.*, 1900, 33, 2584—2586).—Lecithin is best prepared by extracting egg yolk with 96 per cent. alcohol and precipitating with cadmium chloride at 0° ; the precipitate is then extracted with ether, and decomposed by boiling with alcohol and ammonium carbonate. The lecithin separates from the alcoholic solution at -10° , and may be purified by being

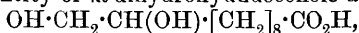
dissolved in chloroform and precipitated with acetone. A further quantity may be obtained from the alcoholic mother liquor. The yield is about 4 per cent. of the yolk. The sample obtained yielded palmitic, stearic, and oleic acids, and an attempt to prepare a sample by fractional precipitation which would only yield one acid proved unsuccessful. The platinichloride when quite dry is insoluble in ether, but dissolves readily after having been moistened with water.

Lecithin, contrary to the statement of Diaconoff (*Annalen*, 1868, 148, 77), can be powdered and preserved in an exhausted vessel.

A. H.

Constituents of Cascarilla Oil and Undecenoic Acid. By HERMANN THOMS (*Chem. Centr.*, 1900, ii, 574—575; from *Verh. Vers. Deutsch. Naturf. Aerzte*, 1899, ii, 648—652).—In cascarilla oil, G. Fendler has found 2.10 per cent. of free acid, 0.30 of eugenol, 10 of a terpene, $C_{10}H_{16}$, boiling at 155—157°, 8.8 of *l*-limonene, 13.2 of *p*-cymene, 10.5 of a sesquiterpene, $C_{15}H_{24}$, boiling at 255—257°, 33 of a sesquiterpene boiling at 260—265°, 11 of an alcohol, $C_{15}H_{23}\cdot OH$, boiling at 280—290°, 10 of compounds of higher boiling point containing oxygen, and 1.1 of resin. The *terpene*, which boils at 155—157°, forms oily additive compounds with HCl and $2Br$, and is not identical with pinene; the *nitrosochloride*, $C_{10}H_{16}\cdot ONCl$, melts at 91—92°, and the *nitrolpiperidide*, $NO\cdot C_{10}H_{16}\cdot C_5NH_{10}$, at 112°. In addition to palmitic and stearic acids, the oil contains *cascarillic acid*, $C_{11}H_{20}O_2$, which distils as an oil; it boils at 268—270°, solidifies at about -18° , has a sp. gr. 0.9324 at 20°, and is scarcely attacked by potassium permanganate. The *amide*, $C_{10}H_{19}\cdot CO\cdot NH_2$, melts at 78°. By the action of fuming nitric acid on cascarillic acid, a small quantity of an unsaturated acid, $C_{11}H_{18}O_4$, is formed; it crystallises in lustrous leaflets and melts at 111°.

Undecenoic acid, $CH_2\cdot CH\cdot [CH_2]_8\cdot CO_2H$, is oxidised by fuming nitric acid at 60°, forming sebacic acid, $CO_2H\cdot [CH_2]_8\cdot CO_2H$, whilst by the action of potassium permanganate at the ordinary temperature it yields a small quantity of κ -dihydroxyundecenoic acid,



and at 0° it forms a hydroxyketonic acid, $OH\cdot CH_2\cdot CO\cdot [CH_2]_8\cdot CO_2H$. The last-named acid reduces Fehling's solution and ammoniacal silver solutions and also forms a *semicarbazone* which melts at 145°; by oxidation, or by hydrolysing the hydroxynitrile obtained by means of hydrogen cyanide, sebacic acid is formed.

E. W. W.

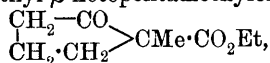
Camphoric Acid. IX. Structure and Configuration of *cis-trans*-Campholytic Acid. By WILLIAM A. NOYES and EDWARD F. PHILLIPS (*Amer. Chem. J.*, 1900, 24, 285—291).—Aminodihydrocampholytic acid (*Abstr.*, 1895, i, 187, 295, 552) in aqueous solution has $[\alpha]_D + 53.7^\circ$; 7.6 parts dissolve in 100 parts of water at 20°. The hydroxydihydrocampholytic acid obtained by its decomposition with nitrous acid has a solubility of 2.05 parts in 100 parts of water at 20°, and $[\alpha]_D + 71.85^\circ$; the *cis-trans*-campholytic acid formed simultaneously has a sp. gr. 1.0166 at 13.2°, 1.0145 at 18°, and 1.0107 at 27.5°, $[\alpha]_D$ being -60.4° , 59.6° , and 58.0° at the same temperatures. β -Bromodihydrocampholytic acid, $C_8H_{14}Br\cdot CO_2H$, obtained

from *cis-trans*-campholytic acid and hydrogen bromide, has $[\alpha]_D + 90.5^\circ$ in 10 per cent. benzene solution, and is apparently identical with the acid formed from hydroxydihydrocampholytic acid and hydrogen bromide ($[\alpha]_D + 93.5^\circ$).

The bearing of these facts on the question of the configuration of campholytic acid is dealt with at some length. W. A. D.

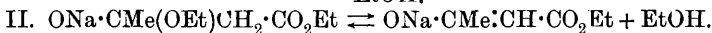
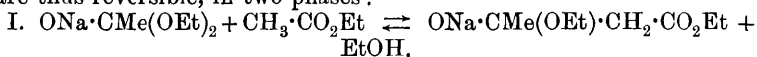
Condensations with Ethyl Acetoacetate and their Reversal. By WILHELM DIECKMANN (*Ber.*, 1900, **33**, 2670—2684).—Although ethyl acetoacetate is only slightly changed by boiling with alcoholic sodium ethoxide (1 mol.) for 2 hours, ethyl ethylacetoacetate methylacetoacetate, and benzylacetoacetate are, under similar conditions, completely resolved into acetic acid and the corresponding alkylacetic ester, $\text{CH}_2\text{R}\cdot\text{CO}_2\text{Et}$ ($\text{R} = \text{Me}, \text{Et}, \text{CH}_2\text{Ph}$); using a smaller proportion of sodium ethoxide (about 15—20 per cent. of that calculated), the hydrolysis is only very partial after 2 hours, although under the same conditions with dialkylacetoacetic esters ($\text{CR}_2\text{Ac}\cdot\text{CO}_2\text{Et}$, $\text{R}_2 = \text{Me}_2, \text{Et}_2, \text{Et}, \text{CH}_2\text{Ph}$) it is complete, acetic acid and a dialkylacetic ester being obtained. These facts are explained by assuming that the ease of decomposition of β -ketonic esters depends on their "acidity," being greatest when this is least. Thus, the "strongly

acid" β -ketopentamethylenecarboxylic ester, $\begin{array}{c} \text{CH}_2-\text{CO} \\ | \\ \text{CH}_2\cdot\text{CH}_2 \end{array} > \text{CH}\cdot\text{CO}_2\text{Et}$, is much more stable towards sodium ethoxide than the closely related "feebly acid" open-chain compound, $\text{CH}_3\cdot\text{CO}\cdot\text{CHEt}\cdot\text{CO}_2\text{Et}$, whilst the "neutral" ethyl α -methyl- β -ketopentamethylenecarboxylate,



is as easily resolved as the "neutral" dialkylacetoacetic esters, $\text{CH}_3\cdot\text{CO}\cdot\text{CRet}\cdot\text{CO}_2\text{Et}$.

The ethyl acetoacetate condensations in presence of sodium ethoxide are thus reversible, in two phases:—



The more "acid" in nature the final β -ketonic ester is, the more stable is its sodium derivative towards alcohol, and hence the less tendency is there to reversal; thus the formation of ethyl acetoacetate from ethyl acetate in presence of sodium ethoxide is much more rapid and complete than that of ethyl dimethylacetoacetate from ethyl acetate and ethyl dimethylacetate, because in the latter case the derivative, $\text{ONa}\cdot\text{CMe}(\text{OEt})\cdot\text{CMe}_2\cdot\text{CO}_2\text{Et}$, initially formed, is very susceptible to decomposition by alcohol. The ease of formation, on the other hand, of, for example, strongly acid diphenylacetoacetic esters from phenylacetoacetic esters (Volhard, *Abstr.*, 1897, i, 422), and of strongly acid, cyclic, β -ketonic-carboxylic esters from adipic and pimelic esters (*Abstr.*, 1894, i, 173) is due to the slight tendency to reversal that exists in these cases.

By the foregoing views, the fact that the decomposition of ethyl dialkylacetoacetates by alcoholic sodium ethoxide is prevented by the presence, in excess compared with the sodium ethoxide

employed, of ethyl acetoacetate or of an ethyl monoalkylacetate, is capable of ready explanation, whilst the need of care to avoid an excess of sodium ethoxide in the Conrad-Limpach method is emphasised. The easy decomposition of dialkylacetoacetic esters by alcoholic sodium ethoxide furnishes, moreover, a means of obtaining dialkylacetic acids which is preferable in many cases to using alkali, because, with the latter, ketonic hydrolysis always occurs.

When ethyl diethylacetoacetate (2 mols.) is heated in absolute ethereal solution for 6 hours with sodium ethoxide (1 mol.) containing only traces of alcohol, ethyl diethylacetate is formed along with *ethyl γ -acetyl- β -diethylacetoacetate*, $\text{CH}_2\text{Ac}\cdot\text{CO}\cdot\text{CEt}_2\cdot\text{CO}_2\text{Et}$, which boils at $255\text{--}260^\circ$, and yields a crystalline *copper* salt melting at 85° ; it is probable that condensation here occurs between the compound $\text{ONa}\cdot\text{CMe}(\text{OEt})_2$, formed by the initial decomposition, and unchanged ethyl diethylacetoacetate (compare Conrad and Gast, *Abstr.*, 1898, i, 512).

The following compounds are new: *Ethyl β -phenyl- α -ethylpropionate*, $\text{CH}_2\text{Ph}\cdot\text{CH}_2\text{Et}\cdot\text{CO}_2\text{Et}$, obtained by boiling ethyl ethylbenzylacetoacetate with alcohol containing a small quantity of sodium, boils at $251\text{--}253^\circ$ (uncorr.). *Ethyl 1-methyl-2-ketohexamethylenecarboxylate*, obtained from ethyl 2-ketohexamethylenecarboxylate and methyl iodide by the Conrad-Limpach method, boils at $110\text{--}111^\circ$ under 12 mm. pressure, and, with boiling alcoholic sodium ethoxide yields ethyl α -methylpimelate, which boils at 140° under the same pressure.

W. A. D.

New Product of the Destructive Distillation of Tartaric Acid. By L. J. SIMON (*Compt. rend.*, 1900, 131, 586—588).—The destructive distillation of tartaric acid in presence of potassium hydrogen sulphate yields about 0.1 per cent. of an acid, $\text{C}_7\text{H}_8\text{O}_3$, which is isomeric, but not identical with the pyrotritaric acid (dimethylfurfurancarboxylic acid) of Wislicenus and Stadnicki (*Bull. Soc. Chim.*, 1868, 10, 489). It softens at about 158° , melts at 164° , and resolidifies at 156° , sublimes readily in white needles or lamellæ, and crystallises from alcohol in prisms, and from water in needles which, after drying at 100° , melt at 164° . It is neutral to helianthin, but acid to phenolphthalein and to litmus; its potassium salt, $\text{C}_7\text{H}_7\text{O}_3\text{K}\cdot 2\text{H}_2\text{O}$, is alkaline to all indicators except blue, C4B. The acid and its potassium salt combine readily with bromine and reduce potassium permanganate and silver nitrate in the cold, but do not reduce Fehling's solution.

C. H. B.

isoPyrotritaric Acid; a New Pyrogenic Product from Tartaric Acid. By L. J. SIMON (*Compt. rend.*, 1900, 131, 618—620. Compare this vol., i, 198).—*isoPyrotritaric acid*, $\text{C}_7\text{H}_8\text{O}_3$, obtained as a by-product in the dry distillation of tartaric acid, is isomeric with the pyrotritaric acid described by Wislicenus and Stadnicki. It develops a violet coloration with ferric salts closely resembling that obtained from salicylic acid; this colour is changed to orange-red by alkalis; it is not affected by heat, but is removed by concentrated acids and reappears on dilution.

The *ferric* salt, $\text{Fe}(\text{C}_7\text{H}_7\text{O}_3)_3\cdot 2\text{H}_2\text{O}$, produced by digesting precipitated ferrichydroxide with a saturated aqueous solution of the acid, forms

deep red crystals giving a red solution. Like ferric salicylate, it may be employed as an indicator in acidimetry. The colour of the solution is not altered by the addition of *isopyrotritaric* acid, whereas salicylic acid turns it violet; the ferric *isopyrotritarate* may therefore be used in estimating salicylic acid; it also serves as a reagent for ferric salts, giving a colour reaction in dilutions of 1/100,000. The potassium salt of *isopyrotritaric* acid gives the same colour reaction as the acid; the oxidation product and the additive compound with bromine obtained from the latter are, however, devoid of this property.

Pyrotartaric acid, the acids of the furfuran series, and pyruvic acid do not give colorations with ferric salts, but the diethyl pyrotartrate obtained from the residues of the distillation of tartaric acid and the last fractions obtained by distilling pyruvic acid under ordinary pressure both exhibit this colour reaction, and contain *isopyrotritaric* acid.

There is some reason for supposing that the new acid is a hydroxy-dihydrobenzoic acid. G. T. M.

Pinolic Acid. By FERDINAND TIEMANN [and MAX KERSCHBAUM] (*Ber.*, 1900, 33, 2661—2670).—A method is given for the preparation of *i*-pinonic acid in quantity.

i-Pinolic acid, $\text{CO}_2\text{H} \cdot \text{CH}_2 \cdot \text{CH} < \begin{smallmatrix} \text{CMe}_2 \cdot \text{CHMe} \\ \text{CH}_2 - \text{CH} \cdot \text{OH} \end{smallmatrix}$ is formed when *i*-pinonic acid is heated with alcoholic potash for 6—7 hours at 185—200°; it crystallises in felted needles melting at 99—100°, boils at 195—205° under 20 mm. pressure, is equally sparingly soluble in hot or cold water, dissolves readily in alcohol, ethyl acetate, or ether. On oxidation with potassium permanganate, it affords *i*-pinonic acid.

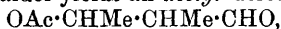
l-Pinolic acid, prepared from *d*-pinonic acid, crystallises in well-formed needles melting at 114—115°. In 33 per cent. alcoholic solution it has a rotation -7° in a 100 mm. tube.

i-Pinocampholenic acid, $\text{CO}_2\text{H} \cdot \text{CH}_2 \cdot \text{CH} < \begin{smallmatrix} \text{CMe}_2 \cdot \text{CMe} \\ \text{CH}_2 - \text{CH} \end{smallmatrix}$, is obtained when crude pinolic acid which has not been subjected to treatment with a current of steam is distilled under reduced pressure; the distillate also contains pinodihydrocampholenolactone. It is a transparent, oily liquid having a faint odour, boils at 140—141° under 13 mm. pressure, has a sp. gr. 0.9925 at 17°, and n_D 1.46702, its molecular refraction being 46.97, and the calculated number 47.34. It yields pinodihydrocampholenolactone when treated with hydriodic acid, and when oxidised with permanganate yields the same products as α -campholenic acid. Active pinocampholenic acid, from *d*-pinonic acid, boils at 136—138° under 10 mm., and at 248—252° under atmospheric pressure. It has a sp. gr. 0.9897 at 20°, n_D 1.47096, and molecular refraction 47.45.

Pinodihydrocampholenolactone, obtained both from pinolic acid and pinocampholenic acid, is a colourless oil with an odour exactly resembling that of dehydrocampholenolactone. It boils at 128—130° under 12 mm., and at 254—257° under atmospheric pressure, has a sp. gr. 1.014 at 18°, n_D 1.4640, and the molecular refraction 45.72, the calculated number being 45.79. When hydrolysed, it yields a hydroxy-acid which does not crystallise, but on distillation yields crystalline pinolic acid.

The foregoing facts are in accordance with Tiemann's formula for pinonic acid, but are scarcely explicable by means of Baeyer's formula. The production of pinic acid, which certainly has the constitution assigned to it by Baeyer (Abstr., 1896, i, 247), is attributed to profound internal change. A. L.

Condensation of Acetaldehyde with Propaldehyde. By F. X. SCHMALZHOFFER (*Monatsh.*, 1900, 21, 671—692. Compare Lieben and Zeisel, Abstr., 1886, 783).—The aldol, $\text{OH}\cdot\text{CHMe}\cdot\text{CHMe}\cdot\text{CHO}$, obtained when a mixture of acetaldehyde and propaldehyde is heated in a sealed vessel with potassium hydrogen carbonate solution, forms a colourless liquid distilling at 92° under 20 mm. pressure; it is appreciably soluble in water and readily in alcohol or ether; when kept for some time, it polymerises to $(\text{C}_5\text{H}_{10}\text{O}_2)_2$, and on continued boiling in a reflux apparatus it loses the elements of water and yields tiglic aldehyde. The aldol yields an *acetyl* derivative,



which distils at $105\text{--}110^\circ$ under reduced pressure, and on reduction yields 1:2-dimethylpropan-1:3-diol, $\text{OH}\cdot\text{CH}_2\cdot\text{CHMe}\cdot\text{CHMe}\cdot\text{OH}$, which distils at 200° under atmospheric pressure or at $112\text{--}115^\circ$ under 20 mm. pressure; its *diacetyl* derivative, $\text{OAc}\cdot\text{CH}_2\cdot\text{CHMe}\cdot\text{CHMe}\cdot\text{OAc}$, distils at $107\text{--}108^\circ$ under 18 mm. pressure. When heated with dilute sulphuric acid, the glycol is converted into methylethylacetaldehyde and the *anhydride* $(\text{C}_5\text{H}_{10}\text{O})_2$, distilling at $180\text{--}185^\circ$ under atmospheric pressure. On oxidation with 1 per cent. permanganate, the glycol yields β -hydroxy- α -methylbutyric acid (compare Rücker, *Ber.*, 1877, 10, 1754), and the aldol when oxidised in a similar manner yields methyl ethyl ketone. Attempts to obtain the oxime of the aldol gave the *oxime* of tiglic aldehyde as an oil distilling at $150\text{--}154^\circ$ under 20 mm. pressure. J. J. S.

Boiling Points of Mixtures of Chloral and Water. By JOSEPH C. CHRISTENSEN (*J. Physical Chem.*, 1900, 4, 585—597).—Tables and curves are given for the boiling points of mixtures of chloral and water, several sets of experiments being recorded. The boiling point of the chloral falls rapidly on addition of water, attaining a minimum for about 4 per cent. of water, it then rises at first very rapidly, but slowly after about 20 per cent. of water has been reached. The readings are, however, only given for the Beckmann thermometer, the actual temperatures not being recorded, whilst no determinations appear to have been made in the neighbourhood of the minimum. L. M. J.

Nomenclature of the Peroxides: Aldehydic Peroxides. By ADOLF VON BAEYER and VICTOR VILLIGER (*Ber.*, 1900, 33, 2479—2487).—The authors suggest that hydrogen peroxide, its acyl derivatives, and their peroxides should be called "hydroperoxide," "peracids," and "peroxides" respectively. Accordingly, the compound $\text{Ph}\cdot\text{CO}\cdot\text{O}_2\text{H}$ is "benzoieperacid," and its anhydride "benzoieperoxide." The term "persulphuric acid" is retained for the substance $(\text{HSO}_4)_2$ and Caro's acid, $\text{HSO}_3\cdot\text{O}_2\text{H}$, is called monosulphoperacid. The paper contains a

list of the peroxides with their designations according to the proposed nomenclature.

Dichloral peroxide hydrate, $O_2[CH(OH) \cdot CCl_3]_2$, obtained by treating chloral either with an ethereal solution of hydrogen peroxide or with Caro's reagent, crystallises from benzene or chloroform in hexagonal leaflets or plates and melts at 122° ; it is freely soluble in ether, forming a compound containing 1 mol. of the solvent, which crystallises in long prisms. The dry substance, when mixed with potassium iodide, evolves oxygen, a small amount of iodine being simultaneously liberated; it is decomposed by a solution of sodium hydrogen carbonate into chloral and hydrogen peroxide.

The pungent explosive substances produced either by treating diethyl or dipropyl ketone with Caro's reagent, or by decomposing diacetone diperoxide with concentrated sulphuric acid, are not simple ketone peroxides as previously stated (this vol., i, 206, 328); they are 'peracids' produced by oxidation either from the ketones or from the acetic acid employed as solvent.

Acetaldehyde becomes peroxidised when treated with a sulphuric acid solution of hydrogen peroxide, and yields an oily product which subsequently solidifies; the oil is probably a diacetaldehyde peroxide hydrate and the solid a diacetaldehyde peroxide; this point has not, however, been definitely settled, owing to the explosive nature of the compounds.

Dibenzaldehydediperoxide, $C_{14}H_{12}O_4$, produced by adding benzaldehyde to a dilute alcoholic solution of hydrogen peroxide and sulphuric acid, crystallises in prisms or needles and decomposes at 202° ; it dissolves in the ordinary organic solvents but is insoluble in water. This substance is the inner anhydride, $CHPh \begin{smallmatrix} \text{O} \cdot \text{O} \\ \diagdown \quad \diagup \\ \text{O} \cdot \text{O} \end{smallmatrix} CHPh$, of the compound, $O_2(CHPh \cdot OH)_2$, obtained by Nef by the action of hydrogen peroxide alone on benzaldehyde (Abstr., 1898, i, 109). Hexamethylenetriperoxidediamine (hexahydroxymethylenediamine, Legler, Abstr., 1886, 327) is conveniently prepared by adding 40 per cent. aldehyde to a solution of ammonium sulphate in commercial hydrogen peroxide at 55° ; this substance results from the action of ammonia on diformaldehyde peroxide hydrate, $OH \cdot CH_2 \cdot O \cdot O \cdot CH_2 \cdot OH$, the constitutional formula, $N:(CH_2 \cdot O \cdot O \cdot CH_2)_3:N$, indicating its mode of formation.

G. T. M.

Semi-Aldehyde of Malonic Acid. By ALFRED WOHL and W. EMMERICH (*Ber.*, 1900, 33, 2760—2764).—When digested with very dilute alkali hydroxide solution, β -chloropropaldehydediethylacetal gives rise to β -hydroxypropaldehydediethylacetal, which, on oxidation with potassium permanganate, yields β -diethoxypropionic acid. When the concentrated aqueous solution of the potassium salt of this acid is gently warmed with excess of sulphuric acid, the two ethoxy-groups are replaced by an oxygen atom, the resulting compound being the semi-aldehyde of malonic acid (aldehydopropionic acid), which was not obtained in sufficient quantity to allow of its boiling point being determined.

β -Hydroxypropaldehydediethylacetal, $OH \cdot CH_2 \cdot CH_2 \cdot CH(OEt)_2$, is a

colourless oil boiling at 98° under 20 mm., and at 118° under 36 mm. pressure.

Methyl β-diethoxypropionate, $\text{CH}(\text{OEt})_2 \cdot \text{CH}_2 \cdot \text{CO}_2\text{Me}$, is a colourless oil which boils undecomposed at 193° and dissolves slightly in water.

T. H. P.

Fermentation of Pentoses. By ERNST L. SALKOWSKI (*Zeit. physiol. Chem.*, 1900, 30, 478—494).—On subjecting xylose and arabinose to putrefactive decomposition, the main products are volatile fatty acids. In the case of arabinose, alcohol is formed as well; in the case of xylose, this does not occur.

W. D. H.

Nature of Inactive Sorbose. By J. H. ADRIANI (*Rec. Trav. Chim.*, 1900, 19, 183—185).—*d*-Sorbose has a rotatory power $[\alpha]_D + 41.8^\circ$ in a saturated 85 per cent. alcoholic solution, and 10 c.c. of the solution contains 0.1713 gram of the compound. A saturated solution of *i*-sorbose in 85 per cent. alcohol contains 0.1223 gram of substance per 10 c.c. When two mixtures of 0.4 gram of *i*-sorbose with 0.5 gram and 0.8 gram respectively of *d*-sorbose are separately treated with 30 c.c. of 85 per cent. alcohol, the two saturated solutions obtained have practically identical rotatory powers and concentrations. From these results, it is concluded that *i*-sorbose is a racemic compound and does not consist of inactive mixed crystals.

N. L.

Solubility of Lime in Saccharine Solutions. By JULIUS WEISBERG (*Bull. Soc. Chim.*, 1900, [iii], 23, 740—745. Compare Abstr., 1899, ii, 748).—The solubility in sugar solutions of different strengths of lime in the three forms of calcium oxide, calcium hydr-oxide, and milk of lime was determined at 15—16°, and the results are given in tabular form. The solubilities are in each case sensibly greater than has been found by previous observers. Of the three forms of lime, calcium oxide is the most, and milk of lime the least, soluble; solutions of the former contain about 28 parts of calcium oxide per 100 parts of sugar, but it is possible to obtain somewhat more concentrated, although unstable, solutions. All the solutions become gelatinous, or deposit lime, on heating, and again become clear on cooling. The results of some preliminary experiments on the solubility of lime in sugar solutions at 80° and 90° are also recorded and compared with Lamy's figures.

N. L.

Trehalose. By IWAN SCHUKOFF (*Zeit. Ver. deut. Zuckerind.*, 1900, 818—823).—When crystallised from water, trehalose ($+ \text{H}_2\text{O}$) begins to soften at 94° and melts completely at 96.5—97.5°. It forms compounds with *lime*, $2\text{C}_{12}\text{H}_{22}\text{O}_{11} \cdot 3\text{CaO}$, and *strontia*, $2\text{C}_{12}\text{H}_{22}\text{O}_{11} \cdot 3\text{SrO}$. Oxidation with nitric acid of sp. gr. 1.15 yields saccharic acid. Bau-mann's method of benzoylation yields a mixture of *tri*- and *tetra*-benzoyltrehalose, whilst by Panormoff's modification of this method, *hepta*- and *octo*-benzoyltrehalose are obtained; all these compounds are readily hydrolysed by normal alcoholic potash.

T. H. P.

Oxycelluloses of Cotton, Flax, Hemp, and Rhea. By LÉO VIGNON (*Compt. rend.*, 1900, 131, 558—560).—Purified cotton, flax, hemp, and rhea-fibre, when treated with potassium chlorate and hydro-

chloric acid, yield almost the same proportion (70 per cent.) of oxycellulose, and the four oxycelluloses thus obtained are practically identical in reducing power and acidic properties with respect to colouring matters such as safranine and methylene-blue, and seem to yield the same osazone. The comparatively small differences observed may be attributed to different degrees of condensation of the $(C_6H_{10}O_5)_n$ molecule, but in other respects the four celluloses seem to be identical.

C. H. B.

Acetyl Derivatives of Cellulose and Oxycellulose. By LÉO VIGNON and F. GERIN (*Compt. rend.*, 1900, 131, 588—590).—The action of acetic anhydride in presence of zinc chloride on purified cotton, and on the oxycellulose prepared from it, yields a tetracetyl derivative which seems to be mixed with some triacetyl derivative. A large quantity of tarry products is, however, formed at the same time, and hence the evidence as to the existence of four hydroxyl groups in cellulose and oxycellulose is not conclusive.

C. H. B.

Reduction of Nitrocelluloses. By LÉO VIGNON (*Compt. rend.*, 1900, 131, 530—532).—When nitrocelluloses and nitro-oxycelluloses are reduced by ferrous chloride, the nitro-group is eliminated, but the aldehyde group is not affected. The nitrocelluloses yield oxycellulose, and this affords further proof that they are really nitro-oxycelluloses (this vol., i, 589). On the other hand, when nitrocelluloses and nitro-oxycelluloses are reduced with ammonium sulphide, the aldehyde group is reduced as well as the nitro-group. The difference between the two reductions is probably due to the fact that the first takes place in presence of an acid and the second in presence of an alkali.

C. H. B.

Action of Silver Oxide on Bromoamines with Tertiary Amino-Groups. By NIC. M. KIJNER (*J. Russ. Phys. Chem. Soc.*, 1900, 32, 381—385).—The action of silver oxide on *aaζ*-trimethylheptyl-dibromoamine (di-*iso*amylidibromoamine), $CHMe_2 \cdot [CH_2]_4 \cdot CMe_2 \cdot NBr_2$, yields acetic acid and an unsaturated hydrocarbon probably having the formula $CHMe_2 \cdot [CH_2]_3 \cdot CH : CMe_2$. Under similar conditions, the dibromo-derivative of the amine obtained by reducing nitrohexanaphthene (see Markownikoff, *Abstr.*, 1899, i, 22) yields an unsaturated hydrocarbon and a bromo-compound boiling at 160—170°.

T. H. P.

Action of Zinc Alkyls on Nitrous Esters and Nitroparaffins. By IWAN I. BEWAD (*J. Russ. Phys. Chem. Soc.*, 1900, 32, 420—454; 455—542).—The action of zinc alkyls on alkyl nitrites and nitroparaffins has been investigated, the conditions of working being as follows: The zinc alkyl (rather more than 2 mols.) was placed in a flask filled with carbon dioxide, ether added, and to the cool solution an ethereal solution of the nitrite or nitro-compound (1 mol.) was added gradually and with continuous shaking. After being left for some time, in some cases several months, during the first portion of which the liquid was kept cool, water was added and the decomposition products studied. For the alkyl nitrites, these products are: Zinc hydroxide; the paraffin corresponding with the radicle of the

zinc alkyl; two alcohols corresponding with the two radicles of the zinc alkyl and of the nitrite; and a β -disubstituted hydroxylamine containing as substituent groups the two alkyl radicles of the zinc alkyl.

The action of zinc ethyl on *isopropyl nitrite* yields ethane, ethyl and *isopropyl alcohols*, together with β -*diethylhydroxylamine*, $\text{NEt}_2\cdot\text{OH}$, which is a colourless liquid with a characteristic smell and a caustic taste, and boils at $132\text{--}132.5^\circ$ under 757 mm. and at $40.5\text{--}41^\circ$ under 10 mm. pressure; it is slightly soluble in water, but mixes in all proportions with the organic solvents, and has the sp. gr. 0.8853 at $0^\circ/0^\circ$ and 0.867 at $20^\circ/0^\circ$; it has the normal molecular weight in very dilute benzene solution, and on cooling it solidifies to a crystalline mass which melts at -3° . The *hydrochloride*, $\text{C}_4\text{H}_{11}\text{ON}\cdot\text{HCl}$, melts at $72\text{--}73^\circ$, whilst the *hydrobromide* forms hygroscopic crystals melting at $55\text{--}56.5^\circ$, and the *hydriodide* crystallises in dendritic growths of prisms melting at $165\text{--}167^\circ$; the *oxalate* melts at $134\text{--}138^\circ$. On reduction, the base yields diethylamine, whilst it is oxidised and turned brown in the air; it reduces solutions of the heavy metals in the cold and itself suffers oxidation, yielding, when copper sulphate is employed, acetaldehyde, ammonia, ethylamine, and diethylamine.

The action of water on the product of the interaction of zinc ethyl and *isoamyl nitrite* yields compounds analogous to the above reaction, and, in addition ethyl *isoamyl ether* and β -ethylhydroxylamine (?).

β -*Dipropylhydroxylamine*, $\text{NPr}_2\cdot\text{OH}$, obtained from zinc propyl and propyl nitrite, forms colourless plates melting at $28.5\text{--}29.5^\circ$, and boiling at $157\text{--}159^\circ$ under 748 mm. and at $69\text{--}70^\circ$ under 17–20 mm. pressure; it has a characteristic odour and a caustic taste, and is only slightly soluble in water, but dissolves in all proportions in the organic solvents. On reduction, it yields dipropylamine, whilst oxidation by means of copper sulphate gives propaldehyde, ammonia, propylamine, and dipropylamine. The *hydrochloride* forms a light, non-hygroscopic, crystalline powder melting at $87\text{--}88^\circ$, the *hydrobromide* a crystalline powder melting at $74\text{--}75^\circ$, and the *hydriodide* hygroscopic, colourless needles or plates.

In the case of the nitro-paraffins, the products obtained by the action of zinc alkyls are: zinc hydroxide; the paraffin and the alcohol corresponding with the radicle of the zinc compound; a nitroparaffin formed from the one used in the reaction by the substitution of the alkyl of the zinc compound for a hydrogen atom; a disubstituted β -hydroxylamine containing two different radicles, one being that of the zinc alkyl and the other a primary, secondary, or tertiary radicle containing as many carbon atoms in the molecule as are present in the nitroparaffin and the radicle of the zinc compound together.

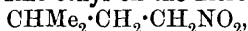
Nitroethane and zinc ethyl give rise to *sec.*nitrobutane, a neutral compound which boils at $180\text{--}181^\circ$, and has the sp. gr. 1.1741 at $0^\circ/0^\circ$, ethyl alcohol and β -ethyl*sec.*butylhydroxylamine, $\text{CHMeEt}\cdot\text{NEt}\cdot\text{OH}$, which is a colourless, viscous liquid with a characteristic odour and a caustic taste; it boils at $155\text{--}158^\circ$ under 756 mm. and at $57\text{--}58^\circ$ under 8 mm. pressure, and has the sp. gr. 0.892 at $0^\circ/0^\circ$ and 0.8757 at $20^\circ/0^\circ$; it is only slightly soluble in water, but dissolves in all proportions in the organic solvents. On reduction, it yields ethyl*sec.*-

butylamine, and on oxidation with ferric chloride or copper sulphate in the cold it gives acetaldehyde, ammonia, methyl ethyl ketone and ethylsec.butylamine. The *hydrochloride* is hygroscopic and melts at 56—57°; the *oxalate* crystallises in nodular aggregates melting at 114—114·5°, and the *acid oxalate* melts at 93—95°.

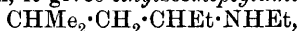
β -Ethylsec.amylhydroxylamine, $\text{CHEt}_2\cdot\text{NEt}\cdot\text{OH}$, obtained together with α -nitropropane, &c., from zinc ethyl and nitropropane, is a viscous liquid with a characteristic smell and a caustic taste, and dissolves in all proportions in the organic solvents, but only to a slight extent in water; it boils at 167—170° under 756 mm., and at 65—67° under 8 mm. pressure, and has the sp. gr. 0·8903 at 0°/0° and 0·8744 at 20°/0°; on cooling, it solidifies to a crystalline mass melting at -8°. On reduction, it yields ethylsec.butylamine, whilst oxidation with ferric chloride converts it into acetaldehyde, ammonia, diethyl ketone, sec.-amylamine and ethylsec.amylamine. The *hydrochloride* of the base forms hygroscopic crystals, and the *hydriodide* a pale yellow, crystalline powder; the *oxalate* melts at 118—119°.

β -Ethyltert.amylhydroxylamine, $\text{CMe}_2\text{Et}\cdot\text{NEt}\cdot\text{OH}$, prepared from zinc ethyl and nitroisopropane, is a thick, colourless liquid which boils at 156—160° under 760 mm. and at 58·5—60·5° under 12 mm. pressure and does not solidify when cooled to -80°; its sp. gr. at 0°/0° is 0·8912. On reduction, it yields ethyltert.amylamine, which is also formed on oxidation together with tert.amylamine and $\beta\beta$ -nitroso-methylbutane. The *hydrochloride* of the base melts at 83°.

β -Ethylsec.heptylhydroxylamine, $\text{CHMe}_2\cdot\text{CH}_2\cdot\text{CHEt}\cdot\text{NEt}\cdot\text{OH}$, obtained by the action of zinc ethyl on the nitropentane,



is a viscous liquid which boils at 91·5—93·5° under 12—13 mm. pressure, and has the sp. gr. 0·8797 at 0°/0° and 0·8641 at 20°/0°. On reduction or oxidation, it gives ethylsec.heptylamine,



which boils at 155—158°, and forms a *hydrochloride* melting at 92—97° and a pale yellow *benzenesulphonamide*. Other products of the oxidation are acetaldehyde, ethyl isobutyl ketone, and traces of isovaleric acid. The *hydrochloride*, which is very hygroscopic and melts at 66—74°, and the *hydrobromide* of the hydroxylamine were prepared.

β -Ethylpropylhydroxylamine, $\text{NEtPr}^a\cdot\text{OH}$, prepared from zinc ethyl and nitromethane, is a viscous liquid similar to, but with a less caustic taste than, its higher homologues; it boils at 143—147° under 765 mm. and at 57—58° under 10—11 mm. pressure, and has a sp. gr. 0·8778 at 0°/0°. Its *hydrochloride* melts at 55—58°. The usual products were obtained on oxidation and on reduction.

β -Propylsec.amylhydroxylamine, $\text{CHMePr}^a\cdot\text{NPr}^a\cdot\text{OH}$, prepared from zinc propyl and nitroethane, boils at about 183° under the ordinary pressure, and at 90·5—92° under 16 mm., and has the sp. gr. 0·8807 at 0°/0° and 0·8654 at 20°/0°. Its *hydrochloride* is very hygroscopic and melts at 63—65°. The normal oxidation products were obtained.

β -Propylsec.hexylhydroxylamine, $\text{CHEtPr}^a\cdot\text{NPr}^a\cdot\text{OH}$, obtained by the action of zinc propyl on nitropropane, boils at about 185° under the ordinary pressure and at 95—97° under 14 mm., and has the sp. gr. 0·8815 at 0°/0° and 0·8637 at 20°/0°. The products of oxidation,

reduction and of the action of sodium on it were studied. The *hydrochloride* melts at 52—54°, and the *hydrobromide* at 44—45°.

β-Propyltert.hexylhydroxylamine, $\text{CMe}_2\text{Pr}\cdot\text{NPr}\cdot\text{OH}$, prepared from zinc propyl and nitroisopropane, is lighter than water and boils at 74—77° under 7—8 mm. pressure. The *hydrochloride* melts at 77—81°.

β-tert.Heptylhydroxylamine, $\text{CEt}_3\cdot\text{NH}\cdot\text{OH}$, obtained by the action of zinc ethyl on chloropicrin, separates from the solution of its hydrochloride as a colourless, microcrystalline powder, melting at 68·5—69·5° and boiling under the ordinary pressure at about 185°; it has a characteristic smell and dissolves slightly in water, and in all proportions in benzene or ether; the *hydrochloride* forms prismatic crystals melting at 146—146·5°. On reduction, it yields *tert.heptylamine* [γ -aminoethylpentane].

The action of zinc ethyl on nitrobenzene gives rise to aniline. With the zinc alkyls, therefore, tertiary nitro-compounds give products different from those obtained with primary or secondary nitro-paraffins; in the former case, either a β -monoalkylhydroxylamine or an amine is formed, whilst in the latter β -dialkylhydroxylamines are always obtained.

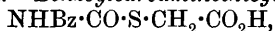
T. H. P.

New Derivative of Glycine. By LUIGI BALBIANO and D. TRASCIATTI (*Ber.*, 1900, 33, 2323—2326).—When a mixture of glycine and glycerol is heated in a sealed tube at 150—170° for 24—30 hours, ammonia and a yellow, amorphous compound, $\text{C}_{22}\text{H}_{34}\text{O}_{13}\text{N}_{10}$, are formed; the latter carbonises at 250° and, when hydrolysed with hydrochloric acid, yields glycine and glycollic acid.

R. H. P.

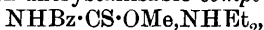
Behaviour of Acylthioncarbamic Esters with Alkyl Iodides and Amines; Benzoyliminothiocarbamic Esters, Acyclic Benzoylpseudocarbamides and Benzoylcarbamides. By HENRY L. WHEELER and TREAT B. JOHNSON (*Amer. Chem. J.*, 1900, 24, 189—221).—*Methyl acetylthioncarbamate*, $\text{NHAc}\cdot\text{CS}\cdot\text{OMe}$, obtained by treating acetyl chloride with lead or potassium thiocyanate and boiling the product with methyl alcohol, or more easily by the action of acetic anhydride on methyl thioncarbamate, crystallises from light petroleum, melts at 79—80°, and is readily soluble in water, alcohol, benzene, or chloroform; when boiled with freshly precipitated mercuric oxide, the sulphur is eliminated. If this compound is left for three weeks in contact with methyl iodide at 40—45°, it is converted into *methyl acetylthiolcarbamate*, $\text{NHAc}\cdot\text{CO}\cdot\text{SMe}$, which crystallises from benzene in fine needles, melts at 145·5—146°, and is easily soluble in hot water or alcohol; the sulphur is not removed by the action of mercuric oxide. *Ethyl acetylthioncarbamate*, $\text{NHAc}\cdot\text{CS}\cdot\text{OEt}$, crystallises from water in prisms, melts at 100—101°, and dissolves readily in alcohol or benzene and sparingly in water; it cannot be converted into the isomeric thiol compound, but when heated at 80—90°, yields ethyl thiolcarbamate. Methyl and ethyl benzoylthioncarbamates may be prepared by treating the product of the action of benzoyl chloride on potassium thiocyanate with alcohol. When methyl benzoylthioncarbamate is heated with methyl iodide at 80—90° for 6 hours in a sealed tube, it yields *methyl benzoylthiolcarbamate*, $\text{NHBz}\cdot\text{CO}\cdot\text{SMe}$, which crystallises

in long prisms, melts at 152—153°, and is not affected by mercuric oxide; if, however, the mixture is heated at 100—110°, decomposition occurs, and a nitrogenous compound free from sulphur is produced, melting at 215°, and crystallising from alcohol in small needles. Ethyl benzoylthioncarbamate shows little, if any, tendency to undergo a molecular rearrangement with ethyl iodide, but if heated with it, benzamide is produced. *Benzoylcarbaminothioglycollic acid*,



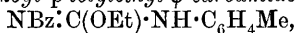
obtained by the action of chloroacetic acid on methyl benzoylthioncarbamate, crystallises in colourless needles, melts at 169—170°, and is not changed when heated with mercuric oxide; if treated with ammonia, it yields benzoylcarbamide melting at 214—215°. *Methyl dibenzoylthioncarbamate*, $\text{NBz}_2 \cdot \text{CS} \cdot \text{OMe}$, formed by the action of benzoic anhydride on the sodium salt of methyl benzoylthioncarbamate, crystallises from light petroleum in colourless plates, melts at 81—82°, and reacts with phenylhydrazine to form hydrogen sulphide and benzoylphenylhydrazine. By the action of methylene iodide on ethyl thioncarbamate, *methylene thiolcarbamate*, $\text{CH}_2(\text{S} \cdot \text{CO} \cdot \text{NH}_2)_2$, is produced, melting at 168—170°. Ethylene thiolcarbamate (Wheeler and Barnes, Abstr., 1899, i, 798) melts at 231—232°. *Trimethylene thiolcarbamate*, $\text{CH}_2(\text{CH}_2 \cdot \text{S} \cdot \text{CO} \cdot \text{NH}_2)_2$, from trimethylene bromide and ethyl thioncarbamate, crystallises from hot water in plates, melts at 177—179°, and dissolves readily in alcohol but only sparingly in benzene. If isobutylene bromide is allowed to react with ethyl thioncarbamate, cyanuric acid and ethyl thiolcarbamate are obtained.

When ethyl benzoylthioncarbamate is dissolved in alcoholic ammonia, hydrogen sulphide and benzoyl- ψ -ethylcarbamide are produced; the last-mentioned substance is converted by dilute hydrochloric acid into benzoylcarbamide, and it furnishes an *aurichloride* which melts at 140°. Methyl benzoylthioncarbamate unites with diethylamine to form an uncrystallisable compound,



which dissolves readily in alcohol or benzene, and is precipitated as an oil by light petroleum. Ethyl benzoylthioncarbamate combines similarly with diisobutylamine, and if the product is heated, hydrogen sulphide, mercaptan, and alcohol are produced, together with a thick oil; when this oil is treated with hydrochloric acid, it yields ethyl chloride and *benzoyldiisobutylthiocarbamide*, $\text{NHBz} \cdot \text{CS} \cdot \text{N}(\text{C}_4\text{H}_9)_2$, which crystallises from alcohol in prisms and melts at 130—132°; if, however, the oil is distilled under 25 mm. pressure, a fraction is obtained boiling at 288—311° under the ordinary pressure, which when rendered alkaline and extracted with ether, furnishes *diisobutylbenzamide* crystallising in prisms and melting at 65°. Methyl benzoylthioncarbamate and diisopropylamine unite to form a substance, $\text{NHBz} \cdot \text{CS} \cdot \text{OMe}, \text{NH}(\text{C}_3\text{H}_7)_2$, which melts at 55—60°, is extremely soluble in benzene or alcohol, and is decomposed by heat with production of hydrogen sulphide, mercaptan, and benzamide. Ethyl benzoylthioncarbamate reacts with benzylamine to form hydrogen sulphide, mercaptan, and *benzoylbenzylcarbamide*, $\text{NHBz} \cdot \text{CO} \cdot \text{NH} \cdot \text{CH}_2\text{Ph}$, melting at 89°; it behaves similarly with aniline, benzoylphenylcarbamide being produced. When a mixture of ethyl benzoylthion-

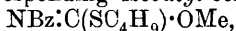
carbamate and *p*-toluidine in molecular proportion is heated on the water-bath, hydrogen sulphide is evolved, and an oil obtained which consists chiefly of *benzoyl-p-tolyethyl-ψ-carbamide*,



and when exposed to the air yields *benzoyl-p-tolylcarbamide*, $\text{NHBz} \cdot \text{CO} \cdot \text{NH} \cdot \text{C}_6\text{H}_4\text{Me}$, melting at 80—81°. If ethyl acetylthioncarbamate is warmed with *p*-toluidine, the products are hydrogen sulphide, *p*-acetyltoluidine, and an oil which was not examined. When ethyl benzoylthioncarbamate is heated with 2:4-dimethylaniline, it furnishes hydrogen sulphide, mercaptan, and *αβ-benzoyl-m-xyllylcarbamide*, $\text{NHBz} \cdot \text{CO} \cdot \text{NH} \cdot \text{C}_6\text{H}_3\text{Me}_2$, which melts at 215—217°. Ethyl benzoylthioncarbamate and *p*-anisidine react with formation of hydrogen sulphide, benzoyl-*p*-anisidine, and *benzoyl-p-methoxyphenyl-carbamide*, $\text{NHBz} \cdot \text{CO} \cdot \text{NH} \cdot \text{C}_6\text{H}_4 \cdot \text{OMe}$, melting at 216—218°, together with small quantities of an oil which, on treatment with hydrochloric acid, yields ethyl chloride, thus indicating the presence of benzoyl-ethyl-*p*-methoxyphenyl-*ψ*-carbamide. By the action of *α*-naphthylamine on methyl benzoylthioncarbamate, hydrogen sulphide is evolved, and an oil produced which furnishes *benzoyl-α-naphthylcarbamide*, melting at 165—166°. When methyl benzoylthioncarbamate is warmed with *β*-naphthylamine, hydrogen sulphide is formed, together with an oil which yields benzoyl-*β*-naphthalide. Ethyl benzoylthioncarbamate and diphenylamine react with formation of hydrogen sulphide and an oil, which is decomposed by hydrogen chloride with separation of diphenylamine. When an ethereal solution of ethyl benzoylthioncarbamate and *o*-phenylenediamine is evaporated, the products are hydrogen sulphide and *dibenzoylphenylenedicarbamide*, $\text{C}_6\text{H}_4(\text{NH} \cdot \text{CO} \cdot \text{NHBz})_2$, which melts at 235°. By the action of phenylhydrazine on methyl benzoylthioncarbamate, hydrogen sulphide is evolved and 3-ethoxy-1:5-diphenyltriazole obtained in colourless needles; this melts at 85—86°, and when heated with hydrochloric acid yields 1:5-diphenyl-3-triazolone. Ethyl acetylthioncarbamate reacts with phenylhydrazine to form hydrogen sulphide and 3-ethoxy-1-phenyl-3-methyltriazole, which crystallises in long prisms and melts at 49°—50°.

The benzoyliminothiocarbonic esters are readily formed by the action of alkyl iodides on the sodium or potassium salts of the benzoylthioncarbamate esters, and are always obtained as oils. When the potassium salt of ethyl benzoylthioncarbamate is treated with ethyl iodide, diethyl benzoyliminothiocarbonate is produced as a colourless oil which boils at 209—212° under 19 mm. pressure; this substance was first prepared by Lössner (Abstr., 1875, 641). The *dimethyl* compound, $\text{NBz} \cdot \text{C}(\text{SMe}) \cdot \text{OMe}$, similarly produced, is converted by dry hydrogen chloride into methyl benzoylthiolcarbamate, whilst by the action of hydrogen sulphide the corresponding thioncarbamate is formed. *Benzoyliminomethylthioethylcarbonate*, $\text{NBz} \cdot \text{C}(\text{SEt}) \cdot \text{OMe}$, boils at 210° under 20 mm. pressure; it reacts with hydrogen chloride with formation of methyl chloride and *ethyl benzoylthiolcarbamate*, $\text{NHBz} \cdot \text{CO} \cdot \text{SEt}$, which crystallises in long, slender prisms, and melts at 105—107°; on attempting to prepare the last-mentioned substance by warming ethyl thiolcarbamate with benzoic anhydride, cyanphenine is produced, together with a compound

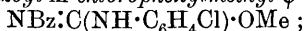
which crystallises in needles, melts at 167—168°, and is probably the polymeric modification of ethyl benzoylthioncarbamate described by Miquel (*Ann. Chim. Phys.*, 1877, [v], 11, 269). When *benzoylimino-methylthiolisopropylcarbonate*, $\text{NBz}\cdot\text{C}(\text{SPr}^\beta)\cdot\text{OMe}$, is treated with hydrochloric acid, *isopropyl benzoylthiolcarbamate*, $\text{NHBz}\cdot\text{CO}\cdot\text{SPr}^\beta$, is obtained which crystallises in prisms and melts at 136—137°. In the same way, the corresponding *isobutyl* compound,



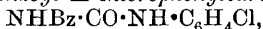
furnishes *isobutyl benzoylthiolcarbamate*, $\text{NHBz}\cdot\text{CO}\cdot\text{SC}_4\text{H}_9$, which crystallises in plates and melts at 115—117°; on the other hand, the *isoamyl* compound, $\text{NBz}\cdot\text{C}(\text{SC}_5\text{H}_{11})\cdot\text{OMe}$, yields *methyl benzoylthioncarbamate*.

Benzoyliminothiocarbonic esters readily react with amines to form benzoyl- ψ -carbamide ethers, which, when treated with hydrochloric acid, are in most cases quantitatively converted into the corresponding benzoylcarbamides. By the action of alcoholic ammonia on benzoyliminomethylthiolisopropylcarbonate, *isopropyl mercaptan* and benzoylmethyl- ψ -carbamide are obtained; the latter compound is identical with that described by Dixon (*Trans.*, 1899, 75, 381), and yields benzoylcarbamide when warmed with hydrochloric acid. *Benzoylmethylethyl- ψ -carbamide*, $\text{NBz}\cdot\text{C}(\text{NHEt})\cdot\text{OMe}$, obtained as an oil by the action of ethylamine on benzoyliminomethylthiolisopropylcarbonate, is similarly converted into $\alpha\beta$ -benzoylethylcarbamide, which melts at 114°. When *isobutylamine* is mixed with benzoyliminomethylthioethylcarbonate, a vigorous action ensues with production of ethyl mercaptan and an oil which yields *benzoylisobutylcarbamide*, $\text{NHBz}\cdot\text{CO}\cdot\text{NH}\cdot\text{C}_4\text{H}_9$; the last-mentioned compound crystallises in long, slender prisms and melts at 115°. When benzoyliminothiolmethylcarbonate and *diisoamylamine* are warmed together until evolution of mercaptan ceases, and the product submitted to the action of hydrogen sulphide, benzonitrile and benzamide are formed, but no appreciable amount of *diisoamylthionmethylcarbamate* is obtained. *Benzoylphenylmethyl- ψ -carbamide*, $\text{NBz}\cdot\text{C}(\text{NHPh})\cdot\text{OMe}$, prepared by the action of aniline on benzoyliminomethylthioethylcarbonate, is converted by hydrochloric acid into benzoylphenylcarbamide. *Benzoylphenylethyl- ψ -carbamide*, $\text{NBz}\cdot\text{C}(\text{NHPh})\cdot\text{OEt}$, is a pale yellow oil.

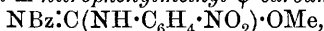
m-Chloroaniline reacts with benzoyliminomethylthioethylcarbonate with formation of *benzoyl-m-chlorophenylmethyl- ψ -carbamide*,



this compound yields *benzoyl-m-chlorophenylcarbamide*,



which crystallises in colourless needles, melts at 200°, and can also be prepared by the action of *m*-chloroaniline on benzoylethylthioncarbamate. *Benzoyl-m-nitrophenylmethyl- ψ -carbamide*,



results from the action of *m*-nitroaniline on benzoyliminomethylthioethylcarbonate; it furnishes *benzoyl-m-nitrophenylcarbamide*,



which crystallises in needles and melts at 231—232°. *Benzoyl- ψ -methyl- ψ -cumylcarbamide*, $\text{NBz}\cdot\text{C}(\text{NH}\cdot\text{C}_6\text{H}_2\text{Me}_3)\cdot\text{OMe}$, is readily

formed on warming benzoyliminothiolmethylcarbonate with ψ -cumidine; *benzoyl- ψ -cumylcarbamide* crystallises from chloroform in long needles and melts at 207°. Benzoyliminomethylthiolisobutylcarbonate and methylaniline react slowly with evolution of mercaptan and formation of a purple-coloured oil. E. G.

Salts of Uric Acid. By FRANCIS W. TUNNICLIFFE and OTTO ROSENHEIM (*Chem. Centr.*, 1900, [ii], 626; from *The Lancet*).—The so-called quadriurates, $C_5H_4O_3N_4M'$, $C_5H_3O_3N_4$, are mixtures of uric acid with its salts. E. W. W.

3-Ethyluric Acid. By E. FRANKLAND ARMSTRONG (*Ber.*, 1900, 33, 2308—2314. Compare E. Fischer, *Abstr.*, 1899, i, 458, and this vol., i, 417).—*Ethyl- ψ -uric acid*, $[CO < \begin{smallmatrix} NH \cdot CO \\ NH \cdot CO \end{smallmatrix} > CH \cdot NH \cdot CO \cdot NHet]$, obtained by the action of ethylcarbimide on uramil in the presence of sodium hydroxide, crystallises from a large quantity of hot water in small, colourless, slender needles, and forms a characteristic *potassium hydrogen* salt, which crystallises in reddish needles, and easily soluble colourless alkali salts, of which the *sodium* (slender needles), *potassium* (large prisms), and *ammonium* (small needles) salts are described. *3-Ethyluric acid*, obtained when the ψ -acid is treated with hydrochloric acid, crystallises in leaflets or long, prismatic needles which do not melt below 350°, and forms the following easily soluble salts: *potassium* (slender needles), *sodium* (well-formed prisms), *ammonium* (slender needles), *potassium hydrogen* (colourless needles), *calcium* and *barium* salts (both clusters of slender needles); when treated with ethyl iodide, it yields a *diethyluric acid*, which crystallises in long, feathery needles, melts and decomposes at 314°, and forms easily soluble neutral alkali salts. 5:7-*Dichloro-2-oxy-3-ethylpurine* is obtained when 3-ethyluric acid is heated at 130—140° in a sealed tube with a mixture of phosphorus oxychloride and pentachloride, it melts at 263—266° (corr.), forms the following colourless soluble salts: *sodium* (slender needles), *potassium* (thin prisms), *ammonium* (plates or needles), *potassium hydrogen* (prisms), and when treated with hydriodic acid and phosphonium iodide yields *iodo-2-oxy-3-ethylpurine*, which crystallises in reddish needles, melts at 247—248° (corr.), and when reduced with zinc dust yields *2-oxy-3-ethylpurine*, which crystallises in colourless prisms, melts at 250—251° (corr.), and forms a crystalline *hydrochloride*, a *hydriodide*, a characteristic *platinichloride*, which crystallises in yellowish-red prisms, an *aureichloride*, and crystalline *potassium* and *ammonium* salts. R. H. P.

Explosiveness of a Mixture of Potassium Cyanide and Nitrite. By J. W. VAN GEUNS (*Rec. Trav. Chim.*, 1900, 19, 186—187).—A mixture of potassium cyanide and nitrite in molecular proportion detonates when heated to about 450°. N. L.

Three Normal Butyltoluenes [Methyl-*n*-butylbenzenes]. By ST. NIEMCZYCKI (*Chem. Centr.*, 1900, ii, 468—469; from *Bull. Acad. Sci. Cracow*, 1900).—The three methylbutylbenzenes prepared by the action of sodium and propyl bromide on *o*-, *m*-, and *p*-xylyl bromides respectively, are colourless liquids and have pleasant odours. Hydro-

carbons boiling above 300° are also formed in the reaction. *o*-Methylbutylbenzene boils at $200-201^{\circ}$, and has a sp. gr. 0.87135 at 18.3° and specific refractive index $[n]_D$ 1.49662. *m*-Methylbutylbenzene boils at $197-198^{\circ}$, and has a sp. gr. 0.86354 at 18.4° and specific refractive index $[n]_D$ 1.49315. *p*-Methylbutylbenzene boils at $198-199^{\circ}$, has a sp. gr. 0.8618 at 14.2° , and specific refractive index $[n]_D$ 1.4912. Kelbe and Baur's *p*-butyltoluene (Abstr., 1884, 301) is not identical with *p*-methyl-*n*-butylbenzene.

E. W. W.

Fluorine Derivatives of Toluene. By FRÉDÉRIC SWARTS (*Chem. Centr.*, 1900, ii, 667—668; from *Bull. Acad. roy. Belg.*, 1900, 414—431. Compare Abstr., 1899, i, 197).—Antimony fluoride (2 mols.) acts very slowly on benzotrichloride (3 mols.) at the ordinary temperature, but forms eventually an almost theoretical quantity of ω -difluorochlorotoluene, $\text{C}_6\text{H}_4\text{ClF}_2$, together with small quantities of ω -fluoro- ω -dichlorotoluene, $\text{C}_6\text{H}_4\text{Cl}_2\text{F}$, and ω -trifluorotoluene, $\text{C}_6\text{H}_4\text{F}_3$. Fluorodichlorotoluene is apparently formed in larger quantity at temperatures below 10° . Difluorochlorotoluene is decomposed by water even at the ordinary temperature, yielding benzoic acid, hydrogen chloride, and hydrogen fluoride. By the action of fuming nitric acid on difluorochlorotoluene at a temperature below 0° , ω -difluoro- ω -chloronitrotoluene, $\text{NO}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{CClF}_2$, together with some *m*-nitrobenzoic acid are formed; a better yield of the former compound and less of the latter is obtained by using a mixture of fuming nitric acid and phosphoric oxide. Difluorochloronitrotoluene is a colourless liquid, boils at 230° , has a sp. gr. 1.4638 at 15° , 1.4555 at 21° , specific refractive index 1.5043 at 21° , and is insoluble in water. It is not readily attacked by water or by nitric acid. Difluorochlorotoluene is destroyed by fuming sulphuric acid, but when dissolved in alcohol it is slowly reduced by sodium amalgam, forming ω -difluorotoluene, CHPhF_2 , which cannot, however, be completely freed from difluorochlorotoluene. Difluorotoluene is a colourless liquid, has a pleasant odour, boils at 133.5° , and, by the action of a small quantity of concentrated sulphuric acid or of water at 200° , is decomposed into benzaldehyde and hydrogen fluoride. By the action of sodium ethoxide, or more slowly by the action of absolute alcohol, difluorotoluene yields ethyl ether, ethyl benzoate, chloroethane, hydrogen fluoride, and hydrogen chloride. ω -Fluoro- ω -dichlorotoluene is a colourless liquid, has a pungent odour, boils at $178-180^{\circ}$, has a sp. gr. 1.3138 at 11° , specific refractive index $[n]_D$ 1.5180, and is decomposed by concentrated sulphuric acid or by boiling water.

ω -Fluoro- ω -dichloronitrotoluene, $\text{NO}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{CCl}_2\text{F}$, prepared by the action of nitric acid and phosphoric oxide on fluorodichlorotoluene, is a nearly colourless liquid, boils at 260° , and has a sp. gr. 1.408 at 18° ; it is only slightly attacked by water, but yields nitrobenzoic acid when boiled with nitric acid of sp. gr. 1.50.

By the replacement of fluorine in the group CF_3 by chlorine, the stability of the compound is diminished, and the chlorine in the fluoro-chloro-derivative obtained may be replaced by a hydroxyl group, but the product very readily loses hydrogen fluoride. A table giving the boiling points of corresponding chloro- and fluoro-derivatives is given. The replacement of one atom of chlorine by fluorine decreases the boiling

point by less than 44° , that is, by less than in the case of the corresponding derivatives of fatty hydrocarbons. E. W. W.

Simultaneous Formation of Isomeric Substitution Products of Benzene. By ARNOLD F. HOLLEMAN [and B. R. DE BRUYN] (*Rec. Trav. Chim.*, 1900, 19, 188—203. Compare Abstr., 1900, i, 387).—The product of the nitration of chlorobenzene at 0° consists of 30.1 per cent. of *o*-chloronitrobenzene and 69.9 per cent. of *p*-chloronitrobenzene, whilst at -30° the proportions are 26.9 and 73.1 per cent. respectively. *m*-Chlorobenzoic acid, when nitrated at 0° , yields 11.4 per cent. of 3-chloro-2-nitrobenzoic acid and 88.6 per cent. of the 3:5-acid; almost identical results are obtained when the nitration is carried out at -30° , the relative proportions of the two acids being 11.5 and 88.5 per cent. respectively. Since the ortho- and para-positions relatively to the chlorine are unoccupied in both chlorobenzene and *m*-chlorobenzoic acid, the formation of different proportions of the nitro-derivatives in the two cases shows that the directing influence of the chlorine on the nitro-group is modified by the presence of carboxyl.

Full details of the analysis of the products of nitration are given in the paper. N. L.

Nitration of *m*-Chlorotoluene. By FRÉDÉRIC REVERDIN and PIERRE CRÉPIEUX (*Ber.*, 1900, 33, 2505—2508).—The two *mononitro*-compounds, obtained by treating *m*-chlorotoluene with concentrated nitric acid, yield on reduction 3-chloro-4-toluidine and 5-chloro-2-toluidine; these bases are separated from each other by the fractional crystallisation of their acetyl derivatives.

3-Chloro-4:6-dinitrotoluene, obtained by nitrating *m*-chlorotoluene with nitric and sulphuric acids, forms pale yellow needles and melts at 91° ; it is volatile in steam. A *chloronitrotoluidine* [3:4:6 or 3:6:4], results from the partial reduction of the preceding compound with an alcoholic solution of ammonium sulphite; it crystallises from benzene and light petroleum in yellow leaflets and melts at 120° ; its *acetyl* derivative melts at 262° .

5-Chloro-2:4-tolylenediamine, obtained from the dinitro-compound by complete reduction with tin and hydrochloric acid, crystallises in colourless leaflets readily soluble in water; it melts at 123° and gives the metadiamine reaction with nitrous acid. The *monoacetyl* derivative melts at 170° ; the diacetyl derivative melts above 250° (compare Morgan, *Trans.*, 1900, 77, 1209).

An additive product, $C_{17}H_{14}O_4N_3Cl$, is formed by treating 3-chloro-4:6-dinitrotoluene with α -naphthylamine and sodium acetate; it crystallises in orange needles and melts at 98° .

4:6-Dinitro-3-tolyl- α -naphthylamine is obtained when this reaction is performed in sealed tubes at 160° ; it crystallises from dilute acetone in brown needles having a metallic lustre and melts at 182° .

4:6-Dinitro-3-tolyl-4'-hydroxyphenylamine, produced in a similar manner from *p*-aminophenol, forms red crystals and melts at 194 — 195° ; it yields a bluish-black colouring matter on heating with sodium sulphide and sulphur. G. T. M.

$\alpha\beta$ -Dichlorostyrenes and some Acetylenes. By FRANZ KUNCHELL and F. GOTSCH (*Ber.*, 1900, 33, 2654—2658).— $\alpha\beta$ -Dichloro-*p*-tolylethyl-

ene, $C_6H_4Me \cdot CCl : CHCl$, made by heating *p*-tolylchloromethylketone (compare this vol., i, 663) with phosphorus pentachloride on the water-bath, the product being subjected to fractional distillation in a vacuum, forms a yellow oil, with an aromatic odour, which boils at $245-250^\circ$, and has a sp. gr. 1.2156 at 20° . α -Chloro-*p*-tolylacetylene, $C_6H_4Me \cdot C : CCl$, prepared by heating the foregoing substance with alcoholic potash, is a limpid, aromatic oil which boils at $145-150^\circ$ under 55 mm. pressure, and has a sp. gr. 1.1142 at 18° .

p-Tolylacetylene, $C_6H_4Me \cdot C : CH$, is easily prepared by allowing sodium to act on an ethereal solution of $\alpha\beta$ -dichloro-*p*-methylstyrene, the reaction being completed by warming for an hour at $40-50^\circ$; it has an odour of anise and fennel, forms crystals melting at 23° , boils at $168-170^\circ$ under atmospheric pressure, and has a sp. gr. 0.912 at 18° .

$\alpha\beta$ -3-Trichloro-4-methylstyrene, $C_6H_3MeCl \cdot CCl : CHCl$, prepared from *o*-chlorotolyl chloromethyl ketone and phosphorus pentachloride, boils at $270-273^\circ$, and has a sp. gr. 1.3808 at 20° . $\alpha\beta$ -Dichloro-2:4-dimethylstyrene, $C_6H_3Me_2 \cdot CCl : CHCl$, boils at $248-249^\circ$, and has a sp. gr. 1.1648 at 19° . $\alpha\beta$ -Dichloro-2:5-dimethylstyrene, $C_6H_3Me_2 \cdot CCl : CHCl$, boils at $247-248^\circ$, and has a sp. gr. 1.1732 at 18° . *p*-Xylylchloroacetylene, $C_6H_3Me_2 \cdot C : CCl$, boils at $134-140^\circ$ under 27 mm. pressure, and has a sp. gr. 1.0743 at 19° . A. L.

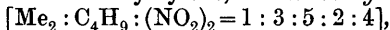
Derivatives of Butylxylene [1:3-Dimethyl-5-butylbenzene]. By ALBERT BAUR-THURGAU (*Ber.*, 1900, 33, 2562-2569).—The *butylxylylidine* [$Me_2 : C_4H_9 : NH_2 = 1 : 3 : 5 : 2$] obtained by reducing solid nitrobutylxylene (m. p. 85° , *Abstr.*, 1891, 1464) with iron and dilute acetic acid, crystallises from light petroleum in large, rhombic plates, melts at 32° , boils at 256° , and has a faint odour of *m*-cresol; the *hydrochloride* and *sulphate* are somewhat sparingly soluble in cold water. The base does not combine with diazo-compounds, but easily yields a *benzylidene* derivative, $C_{12}H_{19}N$, and an *acetyl* derivative which crystallises from dilute alcohol in large plates and melts at 81° ; the *benzoyl* derivative separates from alcohol in slender needles and melts at 233° . On nitration with a mixture of sulphuric acid and 100 per cent. nitric acid, butylxylylidine or its acetyl derivative yields a *nitrobutylxylylidine* [$Me_2 : C_4H_9 : NH_2 : NO_2 = 1 : 3 : 5 : 2 : 4$], which crystallises from alcohol in long, sulphur-yellow needles and melts at 89° ; using an excess of nitric acid, the same dinitrobutylxylylidine

[$Me_2 : C_4H_9 : NH_2 : (NO_2)_2 = 1 : 3 : 5 : 2 : 4 : 6$]

(m. p. 186°) is obtained as is formed by the reduction of trinitrobutylxylene with alcoholic ammonium sulphide (German Patent, 90291; the melting point here given is 170°). On similarly nitrating butylacetoxylidide with an excess of nitric acid, *dinitrobutylacetoxylidide* is obtained; it crystallises from alcohol in leaflets and melts at 192° . Dinitrobutylxylylidine (m. p. 186°) can only be acetylated with acetic anhydride, when it yields a *diacetyl* derivative, $C_{16}H_{21}O_6N_3$, separating from alcohol in granular crystals, and melting at 154° . The *formyl* derivative of butylxylylidine crystallises from alcohol in long, silky needles, and melts at 173° ; the *thiocarbamide* derived from the base separates from alcohol in small needles and melts at 234° , whilst the corresponding *thiocarbimide* separates in thick needles, and melts at 83° .

Attempts to oxidise butylacetoxyhydride to a carboxylic acid with neutral aqueous potassium permanganate failed, but the nitrobutylxylene, melting at 85° , gave, on oxidation in alkaline solution, a *nitrobutylisophthalic acid* $[(\text{CO}_2\text{H})_2 : \text{C}_4\text{H}_9 : \text{NO}_2 = 1 : 3 : 5 : 2]$, separating from alcohol in needles and melting above 300° ; with 20 per cent. nitric acid, however, a *dinitrobutyltoluic acid* melting at 219° is obtained.

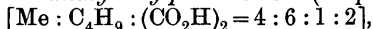
On nitrating solid nitrobutylxylene, a *dinitrobutylxylene*,



is obtained which crystallises from alcohol in yellow needles and melts at 68° ; the same compound is obtained on nitrating the liquid *nitrobutylxylene* $[\text{Me}_2 : \text{C}_4\text{H}_9 : \text{NO}_2 = 1 : 3 : 5 : 4]$ (A. Meyer, *Dis. Basel*, 1894), which boils at 258° under 746 mm., at 158° under 30 mm. pressure, and has a sp. gr. 1.042 at 21° . A second *dinitrobutylxylene* $[\text{Me}_2 : \text{C}_4\text{H}_9 : (\text{NO}_2)_2 = 1 : 3 : 5 : 4 : 6]$ is obtained by eliminating the amino-group, by means of the diazo-reaction, from the dinitrobutylxyldine melting at 186° ; it crystallises from alcohol in stout, slightly yellow needles, from light petroleum in rhombic plates, and melts at 84° . On reducing the dinitrobutylxylene melting at 68° with alcoholic ammonium sulphide, the above-described nitrobutylxyldine (m. p. 89°) is obtained; the latter, again, on nitration, yields dinitrobutylxyldine (m. p. 186°) and, on elimination of the amino-group by the diazo-reaction, the foregoing liquid nitrobutylxylene. On these facts, the structural formulæ attributed to all the foregoing compounds are based. On reduction, the liquid nitrobutylxylene gives a *butylxyldine* $[\text{Me}_2 : \text{C}_4\text{H}_9 : \text{NH}_2 = 1 : 3 : 5 : 4]$, which boils at 246° , and yields a *benzoyl* derivative, $\text{C}_{19}\text{H}_{23}\text{ON}$, melting at 206° ; the *hydrochloride* and *sulphate* are sparingly soluble in water.

Butylxylyl cyanide (m. p. 88°) prepared from butylxyldine (m. p. 32°), has, from the foregoing facts, the structure $[\text{Me}_2 : \text{C}_4\text{H}_9 : \text{CN} = 1 : 3 : 5 : 2]$, and the structure of its dinitro-derivative (m. p. 110° , "cyanide musk," German Patent, 84336) is determined, as well as that of dinitrobutylxylylazimide ("azimide musk," German Patent, 99256).

Since butylxylylaldoxime (*Ber.*, 1898, 31, 2647) on treatment with acetic anhydride yields a *butylxylyl cyanide* which crystallises from light petroleum in white needles, melts at 70° , and is different from that melting at 88° , obtainable from butylxyldine (m. p. 32°), it follows that the structure of butylxylylaldehyde is $[\text{Me}_2 : \text{C}_4\text{H}_9 : \text{CHO} = 1 : 3 : 5 : 4]$. That butylxylyl methyl ketone has an analogous structure is shown by the fact that the derived butylxylyl glyoxylic acid (*Abstr.*, 1898, i, 524), on oxidation with manganese dioxide in sulphuric acid solution, yields a *methylbutylphthalic acid* (m. p. 173°)



which on heating above its melting point loses carbon dioxide and gives rise to a *butyltoluic acid* which crystallises from alcohol in white leaflets, melts at 167° , and, being different from the three known methylbutylbenzoic acids (Effront, *Abstr.*, 1885, 151; Baur-Thurgau, *Abstr.*, 1898, i, 524) has necessarily the structure $[\text{CH}_3 : \text{C}_4\text{H}_9 : \text{CO}_2\text{H} = 1 : 5 : 4]$. The ease with which the carboxyl group in position 3 in methylbutylphthalic acid is displaced on heating is noteworthy, seeing

that the same group in butyltoluic acid [$\text{CH}_3 : \text{C}_4\text{H}_9 : \text{CO}_2\text{H} = 1 : 5 : 3$] is only removed by strongly heating with lime.

Since the methyl ketone prepared from *m*-butyltoluene (*loc. cit.*), yields on oxidation with dilute nitric acid Effront's 2-methyl-4-butylbenzoic acid (m. p. 140°), and on further oxidation with potassium permanganate a butylphthalic acid, it is evident that the ketone residue occupies position 4.

W. A. D.

Action of Iodine and Mercuric Oxide on Styrene and Safrole. By J. BOUGAULT (*Compt. rend.*, 1900, 131, 528—530).—When styrene is treated with iodine and yellow mercuric oxide in presence of alcohol, it yields a highly refractive oily liquid which cannot be distilled without decomposing, and probably has the constitution $\text{CHPhI}\cdot\text{CH}_2\cdot\text{OH}$; when treated with silver nitrate, it yields phenylacetaldehyde. When safrole is treated in the same way, the product of the reaction does not yield an aldehyde on treatment with silver nitrate. It would seem (this vol., i, 472) that all the iodohydrins of the glycols of the general formula $\text{R}\cdot\text{CHI}\cdot\text{CH}_2\cdot\text{OH}$ yield an aldehyde on elimination of hydrogen iodide, and the fact that safrole behaves differently indicates that the generally accepted constitution of this substance is incorrect.

C. H. B.

Double Salts of Bismuth Chloride with some Organic Bases. By O. HAUSER and LUDWIG VANINO (*Ber.*, 1900, 33, 2271—2272).—*Bismuth aniline chloride*, $\text{BiCl}_3\cdot 3(\text{NH}_2\text{Ph}\cdot\text{HCl})$, obtained by dissolving the calculated quantities of bismuth oxide and aniline hydrochloride in alcoholic hydrogen chloride, crystallises in colourless needles, which gradually darken. Similar compounds are formed by *o*- and *p*-toluidine; α - and β -naphthylamine, however, do not yield double salts with bismuth chloride.

If solutions of bismuth oxide and pyridine in alcoholic hydrogen chloride are mixed, a voluminous white precipitate of the *double salt*, $\text{BiCl}_3\cdot 2(\text{C}_5\text{H}_5\text{N}\cdot\text{HCl})$, is produced, which is at first amorphous but gradually becomes crystalline. Quinoline behaves in a similar manner, yielding the *double salt*, $\text{BiCl}_3\cdot 2(\text{C}_9\text{H}_7\text{N}\cdot\text{HCl})$. Both these salts sublime with very little decomposition.

E. G.

New Synthesis of Secondary Amines. By ALFRED TINGLE (*Amer. Chem. J.*, 1900, 24, 276—281).—When ethyl salicylate (1 mol.) and aniline (3 mols.) are heated together for 7 hours, the reaction is very incomplete, and most of the ester can be recovered unchanged; small quantities of salicylaniline, phenol, and a base which is probably ethylaniline, are obtained. Under similar conditions *iso*amyl salicylate and aniline react to about the same extent; phenol is produced, together with a small quantity of a base, which appears to be *iso*-amylaniline.

By the action of dry ammonia on boiling methyl salicylate, dimethylamine and other products are formed.

E. G.

Action of Cyanogen Bromide on Tertiary Amines. II. By JULIUS VON BRAUN (*Ber.*, 1900, 33, 2728—2734; 2965. Compare this vol., i, 430).—The tertiary aromatic amines containing *isopropyl* and allyl radicles react more vigorously with cyanogen bromide than the corre-

sponding propyl and ethyl bases, the reactivity of the *isopropyl* and allyl groups being intermediate between that of methyl and ethyl. The allyl group is most readily detached from the aminic nitrogen whilst the *isopropyl* radicle is retained most tenaciously; in the following series, allyl, methyl, ethyl, propyl, and *isopropyl*, the radicles are arranged in ascending order of their affinity for nitrogen.

Diisopropylaniline, when treated with cyanogen bromide, yields *diisopropylaniline* hydrobromide and *phenylisopropylcyanamide*, an oil boiling at 136—139° under 10 mm. and at 275° under atmospheric pressure. The former compound is produced by the action of *isopropyl* bromide on *diisopropylaniline* at 150° but not from *isopropyl* bromide and *isopropylaniline*.

Propylisopropylaniline, prepared either from propylaniline and *isopropyl* iodide or from *isopropylaniline* and propyl iodide, is a yellow liquid boiling at 216—217°. When treated with cyanogen bromide it yields *phenylisopropylcyanamide* and a deliquescent product which, in all probability, is the hydrochloride of the unaltered base.

Ethylisopropylaniline, obtained from *isopropyl* iodide and ethylaniline, is a colourless liquid boiling at 214—215°; it yields two compounds with platinum chloride, a normal *platinichloride* melting at 199°, and another substance containing less platinum which melts at 159—160°; the latter may be a substituted platinum base. *Ethylisopropylaniline* reacts less vigorously with cyanogen bromide than the amines previously described, the products of reaction are ethyl bromide and *phenylisopropylcyanamide*.

Methylisopropylaniline results from the action of methyl iodide on *isopropylaniline*; it is a colourless oil boiling at 212—213°; the *platinichloride* melts at 196—197°. The base reacts more vigorously with cyanogen bromide than the preceding amine, the products are methyl bromide, *phenylisopropylcyanamide* and a deliquescent salt which could not be analysed.

Methylallylaniline, obtained either from methyl iodide and allylaniline, or from allyl iodide and methylaniline, is a yellow liquid boiling at 214—216°; it reacts very energetically with cyanogen bromide, yielding allyl bromide, *phenylmethylcyanamide*, and an oily substance containing bromine (compare Wedekind, Abstr., 1899, i, 353, 636).

Ethylallylaniline, readily prepared from allyl iodide and ethylaniline, reacts quite as readily with cyanogen bromide, giving rise to allyl bromide, *phenylethylcyanamide* and an oil containing bromine.

Dipropylallylamine and the cyanogen compound yield allyl bromide and dipropylcyanamide.

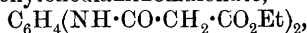
isoPropylallylaniline, prepared from *isopropylaniline* and allyl iodide, is a colourless oil which slowly darkens; it boils at 223—227°; with cyanogen bromide, it furnishes *phenylisopropylcyanamide* and *isoPropylallylaniline* hydrobromide.

G. T. M.

Preparation of Phenylated Guanidines from Diphenylcyanamide. By JULIUS VON BRAUN (*Ber.*, 1900, 33, 2724—2725. Compare this vol., i, 430).—Tetraphenylguanidine is obtained by heating diphenylcyanamide and diphenylamine at 170—180°, its hydrochloride being produced when diphenylamine hydrochloride is employed. β -Tri-

phenylguanidine is produced in a similar manner either from cyananiline and diphenylamine hydrochloride or from diphenylcyanamide and aniline, the yield in the latter case being very poor. A yellow, soluble compound melting at 52° is obtained by heating together ammonia and diphenylcyanamide at high temperatures; this substance is possibly a biguanide. G. T. M.

Formation and Stability of Acid Amides. By RICHARD E. MEYER and G. VON LUTZAU (*Chem. Centr.*, 1900, ii, 562—563; from *Verh. Vers. Deutsch Naturf. Aerzte*, 1899, 86—88).—The carbamides of the meta- and para-series containing closed carbon chains are less stable than those of the ortho-series; thus whilst the former are easily decomposed by heating with fuming hydrochloric acid at 160° , or with alcoholic ammonia at 120° , the latter are not attacked under these conditions. By the action of *p*-phenylenediamine on ethyl malonate, ethyl *p*-phenylenediaminomalonate,



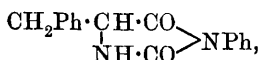
is formed and under certain conditions small quantities of malonamide are also obtained. By the action of *p*-phenylenediamine on ethyl succinate, however, *p*-phenylsuccinimide, $\text{C}_6\text{H}_4\begin{matrix} \text{NH}\cdot\text{CO}\cdot\text{CH}_2 \\ \text{NH}\cdot\text{CO}\cdot\text{CH}_2 \end{matrix}$, is formed, the greater length of the succinic acid chain facilitating the formation of a closed chain, although according to Hjelt (*Abstr.*, 1898, ii, 566) oxalates should show the greatest tendency to form closed chains. E. W. W.

Anilines and Anilides. By FREDERICK D. CHATTAWAY and KENNEDY J. P. ORTON (*Ber.*, 1900, 33, 2396—2400).—*o*-Chloroformanilide, $\text{C}_6\text{H}_4\text{Cl}\cdot\text{NH}\cdot\text{CHO}$, crystallises from light petroleum in plates and melts at 77° . *o*-Chlorobenzanilide, $\text{C}_6\text{H}_4\text{Cl}\cdot\text{NHBz}$, crystallises from alcohol in dilute needles and melts at 99° . *o*-Bromoformanilide melts at 87° . 3:5-Dibromoformanilide crystallises from alcohol in long needles and melts at 100° ; 3:5-dibromoacetanilide crystallises from alcohol in long needles and melts at 231° ; 3:5-dibromobenzanilide crystallises in short, stout prisms and melts at 169° . 4-Chloro-2-bromoaniline crystallises from light petroleum in silky needles, melts at 69° , and boils at 127° under 20 mm. pressure; 4-chloro-2-bromoacetanilide, formed by isomeric change from acetylbroamino-4-chlorobenzene, crystallises from alcohol in rhombic forms and melts at 137° ; 4-bromo-2-chloroacetanilide, prepared in a similar way from acetylchloroamino-4-bromobenzene, melts at 151° , and is hydrolysed to Fittig and Büchner's 2-chloro-4-bromoaniline (*Abstr.*, 1878, 50), which melts at 73° . 2-Bromo-4-nitroacetanilide crystallises from a mixture of benzene and light petroleum in yellow, four-sided prisms and melts at 129° . 2:6-Dibromo-4-nitroacetanilide crystallises in pale yellowish, transparent prisms and melts at 234° ; Nölting, Grandmougin and Michel's compound, melting at 135° (*Ber.*, 1892, 25, 333), is the diacetyl and not the monoacetyl derivative. 2:6-Dichloro-4-nitrodiacetanilide crystallises from cold alcohol in long, silky needles and melts at 140° . 4-Bromo-1-formonaphthalide, $\text{C}_{10}\text{H}_6\text{Br}\cdot\text{NH}\cdot\text{CHO}$, crystallises from chloroform in minute, white needles and melts at 172° .

T. M. L.

Conversion of α -Amino-acids into Phenylhydantoins. By ANTOINE MOUNEYRAT (*Ber.*, 1900, 33, 2393—2396).—The hydantoic acids prepared by the action of phenylcarbimide on α -amino-acids (Paal, *Abstr.*, 1894, i, 332) can be converted into hydantoins by heating with dilute hydrochloric acid. In this way, γ -phenylhydantoin (Guareschi, *Abstr.*, 1892, 828) has been prepared from aminoacetic acid, and Kühn's phenylmethylhydantoic acid was converted into

phenylmethylhydantoin,
$$\begin{array}{c} \text{CHMe}\cdot\text{CO} \\ | \\ \text{NH}\text{---}\text{CO} \end{array} \text{>NPh},$$
 which crystallises from dilute alcohol in needles and melts at 172—173°. Phenylethylhydantoic acid, prepared by the action of phenylcarbimide on α -aminobutyric acid, melts with liberation of gas at 170° (corr.); the hydantoin melts and decomposes at 126—127° (corr.). Phenylisobutylhydantoin,
$$\begin{array}{c} \text{C}_4\text{H}_9\cdot\text{CH}\cdot\text{CO} \\ | \\ \text{NH}\cdot\text{CO} \end{array} \text{>NPh},$$
 and phenylbenzylhydantoin,



were prepared from the hydantoic acids (Fischer, this vol., 646); the latter hydantoin crystallises in needles and melts at 173—174°.

T. M. L.

Convenient Method for the Preparation of Aromatic Thio-carbamides. By JULIUS VON BRAUN (*Ber.*, 1900, 33, 2726—2727).—Substituted thiocarbamides readily result from the action of various oxidising agents on aromatic dithiocarbamates, or mixtures of carbon disulphide and aromatic amines. A mixture of carbon disulphide (1 mol.) and aromatic amine (2 mols.) is shaken up with 3 per cent. hydrogen peroxide and the product extracted with alcohol; the carbamide is obtained from the solution in practically quantitative yield. The method is not applicable to the aliphatic amines.

G. T. M.

Action of Sodium Ethoxide on Ethyl Anilinoacetate. By DANIEL VORLÄNDER and A. T. DE MOULPIED (*Ber.*, 1900, 33, 2467—2470).—When ethyl anilinoacetate is boiled for a short time with alcoholic sodium ethoxide, the anhydride of anilinoacetic acid,

$$\text{NPh} \begin{array}{c} \text{CH}_2\cdot\text{CO} \\ \diagdown \quad \diagup \\ \text{CO}\cdot\text{CH}_2 \end{array} \text{>NPh},$$
 is formed; it is neutral in character.

When ethyl anilinoacetate is heated with dry sodium ethoxide, with or without anhydrous ether or benzene, a product is obtained which melts and decomposes at 190°, dissolves in alkalis, and apparently has

the constitution,
$$\text{NPh} \begin{array}{c} \text{CH}_2\cdot\text{C}\cdot\text{OH} \\ | \\ \text{CO}\text{---}\text{C}\cdot\text{NHPh} \end{array}.$$
 With phenylhydrazine (2 mols.)

it yields an orange-red, crystalline substance melting at 224°; it forms a *monobenzoyl* derivative melting at 168°. It contains no ethoxyl group, for it can be prepared also from methyl anilinoacetate and sodium methoxide; the product in this case is found not to contain methoxyl when examined by Zeisel's method.

C. F. B.

Chlorination of Aceto-*m*-toluidide. By FRÉDÉRIC REVERDIN and PIERRE CRÉPIEU (*Ber.*, 1900, 33, 2503—2504).—A mono-, di-, or

tri-chloro-derivative may be obtained by treating aceto-*m*-toluidide with sodium chlorate and hydrochloric acid in glacial acetic acid, the nature of the product depending on the amount of chlorinating agent employed.

2 : 4-*Dichloro-5-acetotoluidide* crystallises from alcohol in colourless needles and melts at 156°. 2 : 4-*Dichloro-5-toluidine*, prepared by hydrolysing the preceding compound, crystallises from light petroleum and melts at 85°; it is volatile in steam. The *trichloroacetotoluidide* melts at 181°. G. T. M.

Constitution of Metapurpuric Acid. By WALTHER BORSCHKE (*Ber.*, 1900, 33, 2718—2723).—Potassium metapurpurate, when prepared by mixing 2 : 4-dinitrophenol with potassium cyanide in aqueous or alcoholic solution, has a composition agreeing best with the formula $C_7H_2O_4N_3K, 2H_2O$. This salt decomposes on treatment with cold dilute sulphuric acid into nitrous oxide, tarry products, and a small amount of 2 : 4-dinitrohydroxybenzonitrile; it explodes when heated or when moistened with concentrated sulphuric acid.

2 : 4-Dinitrohydroxybenzonitrile is readily prepared by oxidising potassium metapurpurate with dilute nitric acid; it crystallises very readily in pale yellow, lustrous, flattened needles and melts at 125—126°.

With a view of detecting the presence of the group (NH·OH) in purpuric acid, the potassium salt was treated with sodium nitrite and dilute acetic acid; the nitrous acid, however, behaves as an oxidising agent, and the *potassium* salt of 2 : 4-dinitrohydroxybenzonitrile is produced; this substance crystallises with $2H_2O$ in yellow needles, and decomposes explosively on heating. G. T. M.

Purification of Phloroglucinol. By G. S. FRAPS (*Amer. Chem. J.*, 1900, 24, 270—271).—In order to prepare a solution of phloroglucinol sufficiently free from diresorcinol for the estimation of pentosans in vegetable materials, the following method is adopted. Commercial phloroglucinol is extracted with hot hydrochloric acid of sp. gr. 1·06; the hot solution is poured into a larger quantity of hydrochloric acid of the same strength, left for several days, and then filtered; by this means, the greater part of the diresorcinol is removed. E. G.

Occurrence of Phenylethyl Alcohol in Rose Blossoms. By HEINRICH WALBAUM (*Ber.*, 1900, 33, 2299—2302. Compare this vol., i, 509).—Dried rose leaves, when extracted with ether, and fresh rose leaves, when extracted with light petroleum, yield phenylethyl alcohol. R. H. P.

Compounds of Magenta with Acid Colouring Matters having a Basic Chromophore. By ALPHONSE SEYEWETZ (*Bull. Soc. Chim.*, 1900, [iii], 23, 771—784. Compare this vol., i, 356, 522, and 614).—The compounds of magenta with the sulphoconjugated azo-colouring matters, described in the first part of this paper, have already been noticed (this vol., i, 614).

Alkali blue, acid violet 4BN, acid violet 6B, and sulphomagenta

combine with as many mols. of magenta as they contain sulphonic groups, namely, 1, 2, 3, and 4 mols. respectively.

Gallanilic indigo PS, gallanilic green, and rosinduline A all contain one sulphonic group and combine with 1 mol. of magenta, whilst azocarmine A, which contains two sulphonic groups, combines with 2 mols. of magenta. Oxynaphthine contains a hydroxyl and a carboxyl group but no sulphonic group; it combines with 1 mol. of magenta.

Thioflavine S and primuline contain one sulphonic group and combine with 1 mol. of magenta whilst thiazole yellow and erika B contain two sulphonic groups and combine with 2 mols. of magenta.

The results described in this and preceding papers are thus summarised. Among acidic colouring matters having an acid chromophore reinforced or attenuated by the substitution of acid or basic groups, the nitro-colours and colours derived from quinoneoximes, hydroxyketones, and hydroxyquinones combine with 1 mol. of magenta, whatever may be the number of substituting nitro- or hydroxyl groups. In the nitro-derivatives, the presence of sulphonic groups increases the affinity for magenta, whilst with the oxyquinone derivatives the reverse is the case. Derivatives of triphenylmethane of the type of rosolic acid containing only substituted hydroxyl groups combine with 1 mol. of magenta, but if carboxyl groups are also present, the number of mols. of magenta affixed is correspondingly increased. Colouring matters of the phthalein series combine with 2 mols. of magenta. Acidic colouring matters having a basic chromophore rendered acid by the substitution of acid groups, such as sulphonated azo-colours, sulphonated derivatives of triphenylmethane, sulphonic and carboxyl derivatives of quinoneimide, and sulphonated thiazole and azothiazole derivatives combine with as many mols. of magenta as they contain sulphonic groups. In the case, however, of sulphonated azo-colouring matters containing hydroxyl groups in a nucleus other than that containing the sulphonic groups, an additional mol. of magenta is affixed if a sufficient quantity of alkali to react with the hydroxyl groups is added. This result is, perhaps, to be explained by a molecular transformation, as suggested by Farmer and Hantzsch (this vol., i. 122).

N. L.

Resolution of Racemic Amino-acids into Optically Active Components. III. By EMIL FISCHER (*Ber.*, 1900, 33, 2370—2382. Compare this vol., i, 172).—Benzoyl-*d*-leucine, which is laevorotatory in alkaline solution, may be obtained from the racemic compound by means of the cinchonine salt, and the dextrorotatory isomeride can be isolated in the form of quinidine salt.

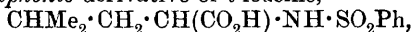
Benzoyl-r-leucine crystallises in colourless, rhombic plates on adding petroleum to the solution in ether, and melts at 137—141° (corr.); it dissolves in 200 parts of boiling water, from which it crystallises in slender needles.

Benzoyl-d-leucine, obtained on resolving the foregoing substance into its active components by means of the cinchonine salt, crystallises in short prisms containing $\frac{1}{2}$ mol. of ether of crystallisation, which is removed at 50°; when containing ether, it melts indefinitely at about

60°, but when free from ether fuses at 105—107° (corr.). It dissolves in 120 parts of boiling water, from which it crystallises in short prisms; an 8.46 per cent. solution in sodium hydroxide (1 mol.) at 20° gives $[\alpha]_D - 6.39^\circ$. The *cinchonine* salt crystallises in aggregates of needles melting at 85°. The *d*-leucine, obtained by hydrolysing the benzoyl derivative with 10 per cent. hydrochloric acid, gave $[\alpha]_D - 16.91^\circ$ in a 4.73 per cent. hydrochloric acid solution at 20°.

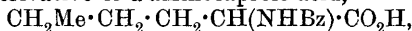
Benzoyl-l-leucine, isolated in the form of quinidine salt, forms crystals containing ether which melt first at 60°, afterwards at 105—107°; $[\alpha]_D$ is +6.59° at 20°. The *quinidine* salt forms colourless prisms and rectangular plates. The *l*-leucine obtained on hydrolysis gave $[\alpha]_D + 15.59^\circ$.

The *benzenesulphononic* derivative of *i*-leucine,



crystallises in prisms which sinter at 140°, and begin to melt at 146° (corr.); the alkali salts are readily soluble in water, and crystallise in needles, whilst the *lead* and *silver* salts, which are also crystalline, dissolve more sparingly. The phenylcarbimide compound of *r*-leucine, $\text{CHMe}_2 \cdot \text{CH}_2 \cdot \text{CH}(\text{CO}_2\text{H}) \cdot \text{NH} \cdot \text{CO} \cdot \text{NHPh}$, crystallises from dilute alcohol in colourless needles, melting and evolving gas at 165° (corr.); it dissolves in about 300 parts of boiling water and in 2 parts of boiling alcohol. The *silver* salt crystallises in small needles.

The *benzoyl* derivative of α -aminocaproic acid,



crystallises in six-sided leaflets and melts at 134° (corr.); the *barium* salt crystallises in small prisms and the *silver* salt in leaflets. The *benzenesulphononic* derivative, $\text{C}_{12}\text{H}_{17}\text{O}_4\text{NS}$, crystallises in aggregates of thin prisms and melts at 125° (corr.). M. O. F.

Resolution of Racemic Amino-acids into Optically Active Components. IV. By EMIL FISCHER and ANTOINE MOUNEYRAT (*Ber.*, 1900, 33, 2383—2393. Compare foregoing abstract).—*Benzoyl-d-phenylalanine*, prepared by resolving the racemic compound into its components with cinchonine, crystallises from 200 parts of boiling water in colourless needles melting at 145—146° (corr.); the alkaline solution has $[\alpha]_D - 17.1^\circ$ at 20°. The *cinchonine* salt crystallises from 100 parts of hot water in colourless needles, and melts at 180—181°. *d-Phenylalanine* crystallises from water in leaflets, and melts, evolving gas, at 283—284° (corr.); a 2 per cent. solution in water has $[\alpha]_D + 35.08^\circ$ at 16°, and a 3.5 per cent. solution in 18 per cent. hydrochloric acid has $[\alpha]_D + 7.07^\circ$. The *phenylcarbimide* compound, $\text{CH}_2\text{Ph} \cdot \text{CH}(\text{CO}_2\text{H}) \cdot \text{NH} \cdot \text{CO} \cdot \text{NHPh}$, crystallises from 300 parts of boiling water in colourless needles melting at 180—181° (corr.); the alkaline solution has $[\alpha]_D + 61.27^\circ$ at 20°. *Benzoyl-l-phenylalanine* has not yet been obtained free from the *lævo*-rotatory isomeride.

r-Benzoyl- α -aminobutyric acid, $\text{CH}_2\text{Me} \cdot \text{CH}(\text{NHBz}) \cdot \text{CO}_2\text{H}$, crystallises from 25 parts of boiling water, sinters at 140°, and melts at 145—146° (corr.). *r- α -Benzenesulphaminobutyric acid* melts at 148—149° (corr.), and resembles the benzoyl derivative in solubility. *d-Benzoyl- α -aminobutyric acid* crystallises from water and melts at 120—121°

(corr.); the solution in sodium hydroxide (1 mol.) has $[\alpha]_D + 30.8^\circ$ at 20° . The *morphine* salt melts at $145-146^\circ$. *d- α -Aminobutyric acid* forms colourless leaflets which melt and decompose at 303° (corr.); a 5.4 per cent. aqueous solution has $[\alpha]_D + 8.0^\circ$. The *hydrochloride* crystallises in needles, and has $[\alpha]_D + 14.51^\circ$ in a 5 per cent. aqueous solution. *l-Benzoyl- α -aminobutyric acid* has $[\alpha]_D - 31.8^\circ$, and in every other respect corresponds with the dextrorotatory compound; the *brucine* salt forms large, transparent crystals which melt at $86-87^\circ$. *l- α -Aminobutyric acid* has $[\alpha]_D - 7.92^\circ$; the *hydrochloride* has $[\alpha]_D - 14.34^\circ$.
M. O. F.

Polymerisation of *p*-Toluonitrile. By JAN PIEPES-PORATYŃSKI (*Chem. Centr.*, 1900, ii, 477; from *Bull. Acad. Sci. Cracow*, 1900).—*p*-Cyanotoline, $(C_6H_4MeCN)_3$, prepared by heating *p*-toluonitrile, *p*-toluic chloride, ammonium chloride, and aluminium chloride at 150° for a long time, crystallises from benzene in white, lustrous, needle-shaped crystals, melts at $276-277^\circ$, and is insoluble in water, very soluble in hot benzene, and slightly so in alcohol. *p*-Toluiline or *tri-p-tolylglyoxaline*, $C_{24}H_{22}N_2$, obtained by the action of zinc dust and boiling glacial acetic acid on *p*-cyanotoline, melts at $234-235^\circ$, is insoluble in water, and forms a *hydrochloride* and a *platinichloride*; in presence of alcoholic potash, it is oxidised by exposure to air, forming a strongly fluorescent solution. One hundred parts of alcohol at 16° dissolve 2.82 of toluiline and on boiling 9.851 parts.
E. W. W.

Boiling and Subliming Points of some Allo-acids. By CARL LIEBERMANN and C. N. RIIBER (*Ber.*, 1900, 33, 2400—2402).—Cinnamic, cinnamylideneacetic, and furfurylacrylic acids, and the corresponding allo-acids, can be distilled or sublimed unchanged in a cathode vacuum; *allocinnamylideneacetic acid* is partially decomposed with loss of carbon dioxide when impure. The following table of temperatures is given:

Cinnamic acid, sublimation point	108°
<i>allo</i> Cinnamic acid, boiling point	95
Cinnamylideneacetic acid, sublimation point.....	145
<i>allo</i> Cinnamylideneacetic acid, sublimation point	130
Furfurylacrylic acid, sublimation point.....	112
<i>allo</i> Furfurylacrylic acid, sublimation point... ..	95

T. M. L.

Bromocoumarins and their Derivatives. III. By HUGO SIMONIS and G. WENZEL (*Ber.*, 1900, 33, 2326—2328. Compare this vol., i, 496).—3:6:8-Tribromocoumarin can be synthesised by treating 6:8-dibromocoumarin dibromide (from 3:5-dibromosalicylaldehyde and acetic anhydride) with cold alcoholic potash. 6-Bromocoumarin dibromide, obtained by the action of bromine on 6-bromocoumarin, is an unstable compound which crystallises in thick prisms, melts at $102-105^\circ$; when treated with alcoholic potash in the cold, it yields 3:6-dibromocoumarin, and when warmed bromocoumarilic acid.

The paper contains a tabular statement of the known bromo-derivatives of coumarin, coumarone, and coumarilic acid.

R. H. P.

Action of Phenylhydrazine and of Hydroxylamine on Ethyl Phenylcyanopyruvate. By EMIL ERLÉNMEYER, *jud.* (*Ber.*, 1900, 33, 2592—2595).—When ethyl β -cyanophenylpyruvate is treated with phenylhydrazine acetate, the *hydrazone* is formed in two isomeric modifications; one crystallises in yellow prisms melting at 107—108°, and the other in fascicular groups of needles melting at 112—113°. The cause of the isomerism of these two forms has not yet been ascertained. When the ester is treated with pure phenylhydrazine, only a small amount of the hydrazone is produced, the greater part of the ester being converted into benzyl cyanide and monoethyl oxalate monophenylhydrazide, a portion of which is then converted into oxalyldiphenylhydrazine.

The *oxime* of ethyl β -cyanophenylpyruvate forms large crystals melting at 119—120°, and has an acid reaction. No separation into optically active components could be effected by means of the cinchonine salt.

A. H.

Formation of Indigotin from Ethyl Anthranilate. By DANIEL VORLÄNDER and C. KOETTNITZ (*Ber.*, 1900, 33, 2466—2467. Compare Henze, this vol., i, 119).—*Ethyl anthranilic acid malonate* (*carb-oxyphenyliminomalonate*), $\text{CO}_2\text{H}\cdot\text{C}_6\text{H}_4\cdot\text{NH}\cdot\text{CH}(\text{CO}_2\text{Et})_2$, is obtained by boiling anthranilic acid with ethyl bromomalonate and water; it melts at 127°, and gives a reddish-brown coloration with ferric chloride. The corresponding *acid* can be obtained from it by hydrolysis, and the *triethyl ester* by condensing ethyl anthranilate with ethyl bromomalonate; these melt at 185° and 122—124° respectively. All yield indigotindisulphonic acid when heated with a large quantity of concentrated sulphuric acid, or indigotin when fused with caustic potash, the triethyl ester, however, reacting less readily than the other compounds.

C. F. B.

Formation of Indigotin from Woad. By MARTINUS W. BEIJERINCK (*Proc. K. Akad. Wetensch. Amsterdam*, 1900, 3, 101—116).—The view formerly expressed that woad contains free indoxyl is now found to be incorrect (this vol., i, 230, 403); this substance is really present in an unstable compound called *isatan*, and is set free by the action of an enzyme, *isatase*. On extracting woad leaves with dilute acids, a solution is obtained which remains unchanged in the air, although indoxyl dissolved in acid of the same strength is oxidised to indigotin; the difference is due to the fact that the acid extract of the plant contains *isatan*, which is stable under these conditions. A solution containing 2—3 per cent. of oxalic acid may be employed in extracting *isatan* from woad leaves; in more dilute acid, the *isatase* becomes active, whereas stronger acid decomposes the substance, yielding indoxyl and brown decomposition products. Dilute solutions of other acids and of acid salts may also be employed in the extraction.

Indican is not affected by alkalis, whereas *isatan* is decomposed even in dilute alkaline solutions and by feebly alkaline salts, such as

disodium hydrogen phosphate or ammonium carbonate. Both indican and isatan are decomposed by acids, the latter also by boiling with acid salts.

Isatase is found in the residue obtained by extracting the disintegrated plant first with alcohol and afterwards with water. Whereas isatan is restricted to the growing parts, isatase is found throughout the plant, and its distribution in the cell is similar to that of the indigo enzymes.

Isatase acts on isatan only in neutral or feebly acid solution, the optimum temperature of reaction being 48–50°; at 70°, the enzyme is completely destroyed. It does not act on indican; isatan, on the other hand, is not decomposed by indigo enzymes and ordinary bacteria.

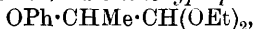
Indoxyl is readily produced from woad by extracting the young leaves with a 0.5 per cent. solution of disodium hydrogen phosphate.

G. T. M.

Synthesis and Degradation in the Coumarone Series. By RICHARD STOERMER (*Annalen*, 1900, 312, 237–336; 313, 79–97. Compare Abstr., 1895, i, 464; 1897, i, 526).—The introductory portion of the paper deals with comparatively recent syntheses in the coumarone series, including the condensation of aryloxyacetals under the influence of zinc chloride dissolved in glacial acetic acid.

In preparing coumarone from phenoxyacetal by the author's method, and likewise when the condensation is effected by means of fused oxalic acid, the yield is greatly reduced by the production of a polymeride. This substance, after several crystallisations from dilute acetic acid, forms a yellowish-brown powder which melts between 80° and 100°, and decomposes at 170–180°; it dissolves very readily in ether, benzene, and chloroform, but is less soluble in alcohol, particularly when hot. Destructive distillation resolves it into phenol, coumarone, and water, in which respect it differs from α -paracoumarone, which yields only traces of phenol when distilled; moreover, determinations of molecular weight agree more closely with the expression $(C_8H_6O)_6$ than with $(C_8H_6O)_4$, or with $(C_8H_6O)_8$, which represent α - and β -paracoumarone respectively.

[With KISSEL.]—1-Methylcoumarone $C_6H_4 \begin{smallmatrix} \diagup O \\ \diagdown CH \end{smallmatrix} \gg CMe$, prepared from α -phenoxypropionacetal, is a colourless liquid having an agreeable odour; it boils at 189–191°, has a sp. gr. 1.0505 at 14°, and the refractive index 1.5495 at 15°. *α -Phenoxypropionacetal*,



obtained from α -bromopropacetal, phenol, and sodium ethoxide in an autoclave at 200–210°, boils at 131–132° under 14 mm.; *α -phenoxypropionaldehyde*, $C_6H_5 \cdot OCHMe \cdot CHO$, boils at 99–101° under 16 mm. pressure, and yields the *oxime* and *semicarbazone* melting at 110° and 161.5° respectively.

2-Methylcoumarone, $C_6H_4 \begin{smallmatrix} \diagup O \\ \diagdown CMe \end{smallmatrix} \gg CH$, derived from phenoxyacetone (Abstr., 1895, i, 464), has been already described by Hantzsch (Abstr., 1886, 707); it boils at 193–194°, has a sp. gr. 1.0596 at 11°,

and the refractive index $[n]_D$ 1.5535 at 16°. It is fairly stable towards concentrated sulphuric acid, being converted but slowly into a polymeride, $(C_9H_8O)_4$; this differs from the substance which accompanies 2-methylcoumarone when prepared from phenoxyacetone and sulphuric acid, and has the formula $(C_9H_8O)_6$.

4-Methylcoumarone, 5-methylcoumarone, and 6-methylcoumarone, $C_6H_3Me \begin{smallmatrix} \diagup O \\ CH \diagdown \end{smallmatrix} CH$, prepared from the three tolyloxyacetals, have been already described (Stoermer, Abstr., 1897, i, 527).

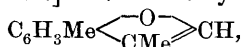
Of the fifteen possible dimethylcoumarones, only the 2:4-dimethylcoumarone of Hantzsch and Lang (Abstr., 1886, 706) has been known hitherto; the authors have increased this number to eleven.

1:4-Dimethylcoumarone, $C_6H_3Me \begin{smallmatrix} \diagup O \\ CH \diagdown \end{smallmatrix} CMe$, boils at 211—213°, has a sp. gr. 1.0491 at 10°, and refractive index 1.5396 at 15°. *p-Cresoxypropacetal*, $C_6H_4Me \cdot O \cdot CHMe \cdot CH(OEt)_2$, boils at 272°, and *p-cresoxypropaldehyde*, $C_6H_4Me \cdot OCHMe \cdot CHO$, boils at 109—111° under 13 mm. pressure, and yields an *oxime* and *semicarbazone* which melt at 90—91° and 152° respectively; *p-cresoxypropionic acid*, $C_6H_4Me \cdot O \cdot CHMe \cdot CO_2H$, melts at 97°.

1:5-Dimethylcoumarone, $C_6H_3Me \begin{smallmatrix} \diagup O \\ CH \diagdown \end{smallmatrix} CMe$, prepared from the aldehyde, $CHO \cdot C_6H_3Me \cdot O \cdot CHMe \cdot CO_2H$, and alcoholic soda at 190°, is a colourless oil which boils at 217—218°, and forms the *picrate* melting at 58—59°; it has a sp. gr. 1.051 at 12°, and refractive index 1.5541 at 15°. When prepared from *m-cresoxypropacetal*, the coumarone boils at a lower temperature, and yields a *picrate* which melts at 48—49°; this is probably due to admixture with 1:3-dimethylcoumarone. *m-Cresoxypropacetal* boils at 271°, and *m-cresoxypropaldehyde* boils at 119—120° under 18 mm. pressure, and yields an *oxime* and *semicarbazone* which melt at 103° and 161° respectively; *m-cresoxypropionic acid* melts at 105°.

1:6-Dimethylcoumarone, $C_6H_3Me \begin{smallmatrix} \diagup O \\ CH \diagdown \end{smallmatrix} CMe$, boils at 208—209°, has a sp. gr. 1.060 at 11°, and refractive index 1.5385 at 15°. *o-Cresoxypropacetal* boils at 139—140° under 15 mm. pressure, and *o-cresoxypropaldehyde* boils at 105—107° under 13 mm. pressure, and yields an *oxime* which melts at 113—114°; *o-cresoxypropionic acid* melts at 93°.

[With HERMES and GROSS.]—2:4-Dimethylcoumarone,



first prepared by Hantzsch and Lang (*loc. cit.*), boils at 218—220° under 747 mm. pressure, and has an intense, persistent odour; it has a sp. gr. 1.0445 at 11°, and refractive index 1.5500 at 16°. The *picrate* melts at 108°. *p-Cresoxyacetone*, $C_6H_4Me \cdot O \cdot CH_2 \cdot COMe$, boils at 255°, and yields an *oxime*, *phenylhydrazone*, and *semicarbazone* melting at 62°, 90°, and 187° respectively.

2:5-Dimethylcoumarone, $C_6H_3Me \begin{smallmatrix} \diagup O \\ CMe \diagdown \end{smallmatrix} CH$, a highly refractive

liquid having the odour of peppermint, boils at 222° , has a sp. gr. 1.0456 at 20° and a refractive index 1.5505 at 20° ; the *picrate* melts at 76° . *m-Cresoxyacetone* boils at 248° , and yields a *semicarbazone* melting at 147° ; the *oxime* and *phenylhydrazine* are oils.

2:6-Dimethylcoumarone, $C_6H_3Me \begin{smallmatrix} \text{O} \\ \diagup \text{CMe} \diagdown \end{smallmatrix} CH$, boils at $216-217^{\circ}$ (corr.), and yields a *picrate* which melts at 68° . *o-Cresoxyacetone* boils at $240-241^{\circ}$, and yields a *semicarbazone* melting at 178° ; the *oxime* and *phenylhydrazine* are oils.

4:6-Dimethylcoumarone, 4:5-dimethylcoumarone, and 3:6-dimethylcoumarone, $C_6H_2Me_2 \begin{smallmatrix} \text{O} \\ \diagup \text{CH} \diagdown \end{smallmatrix} CH$, have been already described by the author as *op*-, *mp*-, and *om*-dimethylcoumarones respectively (Abstr., 1897, i, 527); the properties of the corresponding acetals and aldehydes were recorded at the same time.

3:5-Dimethylcoumarone, $C_6H_2Me_2 \begin{smallmatrix} \text{O} \\ \diagup \text{CH} \diagdown \end{smallmatrix} CH$, boils at 219° , has a sp. gr. 1.037 at 20° , and refractive index 1.5485 at 21° ; the *picrate* melts at 61.5° . *m-Xylenoxyacetal*,

$C_6H_3Me_2 \cdot O \cdot CH_2 \cdot CH(OEt)_2$ [$Me_2 : O = 1 : 3 : 5$], boils at $287-288^{\circ}$; the *aldehyde hydrate* melts at 68° , and yields an *oxime* which melts at 100.5° .

[With BOES.]—5:6-Dimethylcoumarone, $C_6H_2Me_2 \begin{smallmatrix} \text{O} \\ \diagup \text{CH} \diagdown \end{smallmatrix} CH$, boils at 218° , has a sp. gr. 1.038 at 20° , and refractive index 1.5478 at 20° ; the *picrate* melts at 63° . *o-Xylenoxyacetal* (vicinal) boils at 165° under 15 mm. pressure; the *aldehyde hydrate* melts at 75° , and forms an *oxime* and *semicarbazone* melting at 106° and 184° respectively.

4-Ethylcoumarone, $C_6H_3Et \begin{smallmatrix} \text{O} \\ \diagup \text{CH} \diagdown \end{smallmatrix} CH$, has been described by Stoermer and Schroeder (Abstr., 1897, i, 527) as *p*-ethylcoumarone; the properties of the corresponding acetal and aldehyde have been also recorded.

6-Ethylcoumarone, $C_6H_3Et \begin{smallmatrix} \text{O} \\ \diagup \text{CH} \diagdown \end{smallmatrix} CH$, boils at 215° , has a sp. gr. 1.033 at 24° , and refractive index 1.538. *o-Ethylphenoxyacetal*, $C_6H_4Et \cdot O \cdot CH_2 \cdot CH(OEt)_2$, boils at 275° .

2:4:5-Trimethylcoumarone, $C_6H_2Me_3 \begin{smallmatrix} \text{O} \\ \diagup \text{CMe} \diagdown \end{smallmatrix} CH$, boils at $249-250^{\circ}$, and has a penetrating odour suggesting camphor and peppermint; when cooled artificially, it crystallises in rectangular plates melting at 40.5° . The *picrate* melts at $84-85^{\circ}$. *o-Xylenoxyacetone*,

$C_6H_3Me_2 \cdot O \cdot CH_2 \cdot COMe$ [$Me_2 : O = 1 : 2 : 4$], boils at $272-273^{\circ}$; the *semicarbazone* and *oxime* melt at 164.5° and 70° respectively.

[With GROSS.]—2:3:6-Trimethylcoumarone, $C_6H_2Me_3 \begin{smallmatrix} \text{O} \\ \diagup \text{CMe} \diagdown \end{smallmatrix} CH$, melts at 55° , and boils at 243° (corr.); the *picrate* melts at 98° . *p-Xylenoxyacetone* [$Me_2 : O = 1 : 4 : 5$] boils at 261° ; the *semicarbazone* and *oxime* melt at 182° and 132° respectively.

2 : 4 : 6-*Trimethylcoumarone*, $\text{C}_6\text{H}_2\text{Me}_3 \begin{smallmatrix} \text{O} \\ \diagup \quad \diagdown \\ \text{CH} \end{smallmatrix} \text{CH}$, boils at 232° (corr.), and has a sp. gr. 1.007 at 16° ; the picrate melts at 66° . *as-m-Xylenoxyacetone* [$\text{Me}_2\text{O} = 1 : 3 : 4$] boils at 263° ; the *oxime* and *semicarbazone* melt at 133° and 145° respectively.

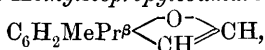
3 : 4 : 6-*Trimethylcoumarone*, $\text{C}_6\text{HMe}_3 \begin{smallmatrix} \text{O} \\ \diagup \quad \diagdown \\ \text{CH} \end{smallmatrix} \text{CH}$, has been already described as 1 : 3 : 4-trimethylcoumarone (*loc. cit.*).

[With VON FINCKH.]—*Trimolecular 3:4:6-trimethylcoumarone*, $(\text{C}_{11}\text{H}_{13}\text{O})_3$, a bye-product in the condensation of ψ -cumenoxyacetal, crystallises from hot glacial acetic acid in slender, white needles, and melts at 168° ; distillation resolves it into trimethylcoumarone and ψ -cumenol.

4-*isopropylcoumarone*, $\text{C}_6\text{H}_3\text{Pr}^i \begin{smallmatrix} \text{O} \\ \diagup \quad \diagdown \\ \text{CH} \end{smallmatrix} \text{CH}$, boils at 235° , has a sp. gr. 1.055, and refractive index 1.5499 at 19.4° . *p-isopropylphenoxyacetal*, $\text{C}_6\text{H}_4\text{Pr}^i \cdot \text{O} \cdot \text{CH}_2 \cdot \text{CH}(\text{OEt})_2$, boils at $287\text{--}288^\circ$; the *aldehyde hydrate* is an oil, and yields a *semicarbazone* and *thiosemicarbazone* melting at $127\text{--}128^\circ$ and 95° respectively.

1 : 3 : 4 : 6-*Tetramethylcoumarone*, $\text{C}_6\text{HMe}_4 \begin{smallmatrix} \text{O} \\ \diagup \quad \diagdown \\ \text{CH} \end{smallmatrix} \text{CH}$, solidifies at 18° and boils at $241\text{--}242^\circ$. ψ -*Cumenoxypropionacetal*, $\text{C}_6\text{H}_2\text{Me}_3 \cdot \text{O} \cdot \text{CHMe} \cdot \text{CH}(\text{OEt})_2$, boils at $159\text{--}160^\circ$ under 16 mm. pressure.

[With GROSS.]—3 : 6-*Methylisopropylcoumarone*,

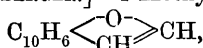


boils at $241\text{--}242^\circ$, has a sp. gr. 1.0145 and refractive index 1.5363 at 16° . *Thymoxyacetal*, $\text{C}_6\text{H}_3\text{MePr}^i \cdot \text{O} \cdot \text{CH}_2 \cdot \text{CH}(\text{OEt})_2$, boils at $280\text{--}281^\circ$.

6 : 3-*Methylisopropylcoumarone*, $\text{C}_6\text{H}_2\text{MePr}^i \begin{smallmatrix} \text{O} \\ \diagup \quad \diagdown \\ \text{CH} \end{smallmatrix} \text{CH}$, boils at $238\text{--}240^\circ$, has a sp. gr. 1.0166, and refractive index 1.5294 at 17° . *Carvacrylacetal* is a colourless oil, and *carvacrylacetaldehyde*, $\text{C}_6\text{H}_3\text{MePr}^i \cdot \text{O} \cdot \text{CH}_2 \cdot \text{CHO}$, yields a *semicarbazone* melting at 253° .

4-*tert. Butylcoumarone*, $\text{CMe}_3 \cdot \text{C}_6\text{H}_3 \begin{smallmatrix} \text{O} \\ \diagup \quad \diagdown \\ \text{CH} \end{smallmatrix} \text{CH}$, boils at $238\text{--}241^\circ$; in preparing it from butylphenoxyacetal, a considerable proportion of butylphenol is regenerated, so that the yield is very small.

[With PAUL SCHRECKENBERGER.]—1-Methyl- β -naphthafuran,



melts at 59° , and has been described by Hantzsch (*loc. cit.*); the *picrate* melts at 156° . β -*Naphthoxyacetone*, $\text{C}_{10}\text{H}_7 \cdot \text{O} \cdot \text{CH}_2 \cdot \text{CO} \cdot \text{CH}_3$, crystallises in lustrous leaflets and melts at 78° ; the *oxime*, *phenylhydrazone*, and *semicarbazone* melt at 123° , 154° , and 203° respectively. 2-Methyl- α -naphthafuran, $\text{C}_{10}\text{H}_6 \begin{smallmatrix} \text{O} \\ \diagup \quad \diagdown \\ \text{CMe}_6 \end{smallmatrix} \text{CH}$, has been also described by Hantzsch; it boils at $296\text{--}299^\circ$.

[With O. RICHTER and K. P. GRÄLERT.]—1 : 2-*Dibromocoumarone*, $\text{C}_6\text{H}_4 \begin{smallmatrix} \text{O} \\ \diagup \quad \diagdown \\ \text{CBr} \end{smallmatrix} \text{CH}$, prepared by the action of bromine on bromo-

coumarone in carbon disulphide, melts at 27° and boils at 269—270°; further treatment with bromine converts it into *tribromocoumarone*, $C_8H_5OBr_3$, which crystallises from alcohol in lustrous needles, melts at 85°, and boils at 315—320°. Both derivatives are indifferent towards silver oxide, even when heated with it at 150° in sealed tubes; concentrated nitric acid converts the dibromide into *dibromonitro-coumarone*, $C_8H_3O_8NBr_2$, which crystallises from alcohol in white needles melting at 188°.

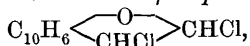
Trichlorocoumarone, $C_8H_5OCl_3$, obtained when chlorine is passed into an ethereal solution of chlorocoumarone, crystallises from alcohol in long, white needles melting at 78° and boils at 258—260° without decomposing. The conditions under which this compound is produced are not fully specified, the additive dichloro-derivative of chlorocoumarone obtained under ordinary conditions being resolved on distillation into hydrogen bromide and 1:2-dichlorocoumarone, $C_8H_4\begin{smallmatrix} O \\ \diagup \diagdown \\ CCl \end{smallmatrix}CCl$, which crystallises from alcohol in white leaflets melting at 25—26°, and boils at 226—227°. The authors have also obtained a *dichlorocoumarone*, $C_8H_4OCl_2$, and a *tetrachlorocoumarone*, $C_8H_4OCl_4$, of unknown constitution; these melt at 42—43° and 131° respectively, and a third *dichlorocoumarone*, $C_8H_4OCl_2$, probably the 1:4-derivative, melts at 72°, and boils above 230°. Chlorocoumarone boils at 199—202°, and not at 215—217°, as stated by Krämer and Spilker (Abstr., 1890, 496).

[With HELBIG.]—4-*Bromocoumarone*, $C_8H_3Br\begin{smallmatrix} O \\ \diagup \diagdown \\ CH \end{smallmatrix}CH$, prepared by heating bromosalicylaldehyde, chloroacetic acid, and alcoholic potash in sealed tubes at 180°, is a pale yellow oil with agreeable odour, boils at 226°, has a sp. gr. 1.593 at 15°, and refractive index 1.6084 at 15°.

Bromocoumarilic acid, $C_8H_3\begin{smallmatrix} O \\ \diagup \diagdown \\ CH \end{smallmatrix}C\cdot CO_2H$, produced in small quantity when the above-mentioned mixture is heated at 198—200°, is a white, crystalline powder which melts at 253° and sublimes in needles. *Bromoaldehydophenoxyacetic acid*, $CHO\cdot C_6H_3Br\cdot O\cdot CH_2\cdot CO_2H$, a bye-product in the formation of 4-bromocoumarone, melts at 163—164° and sublimes in highly lustrous needles. *Bromocoumaroxyacetic acid*, $CO_2H\cdot CH:CH\cdot C_6H_3Br\cdot O\cdot CH_2\cdot CO_2H$, crystallises from hot water in yellowish needles melting at 255—256°.

[With HANS BAUER.]—4-*Chlorocoumarone*, $C_8H_3Cl\begin{smallmatrix} O \\ \diagup \diagdown \\ CH \end{smallmatrix}CH$, boils at 215—217°, has a sp. gr. 1.262 at 16°, and refractive index 1.5778 at 16°. *Chloraldehydophenoxyacetic acid*, $C_8H_7O_4Cl$, separates from hot water in lustrous, white crystals and melts at 169—170°. 4:1-*Chlorocoumarilic acid*, $C_6H_3Cl\begin{smallmatrix} O \\ \diagup \diagdown \\ CH \end{smallmatrix}C\cdot CO_2H$, sublimes in white needles and melts at 258°. 6-*Chlorocoumarone*, C_8H_5OCl , boils at 210—212°.

[With GRÄFENHAN.]—1:2-*Dichloro-β-naphthahydrofuran*,



obtained on passing chlorine into a solution of β-naphthafuran in ether, melts at about 74°, and loses hydrogen chloride when exposed

to air; when heated with pyridine or alcoholic potash, it yields 2-chloro- β -naphthafuran, $C_{10}H_6 \begin{smallmatrix} \text{O} \\ \diagup \text{CH} \diagdown \end{smallmatrix} \text{CCl}$, which crystallises from alcohol in lustrous, white leaflets, and melts at 55° . Trichloronaphthafuran, $C_{12}H_5OC_3Cl_3$, prepared from β -naphthafuran by the action of excess of chlorine, is a white, microcrystalline powder which melts at 144° .

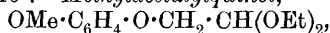
2:6(17)-Dibromo- β -naphthafuran, $C_{12}H_6OBr_2$, formed when bromine acts on β -naphthafuran, even when the latter is in excess, crystallises from alcohol in woolly needles and melts at 82° ; oxidation gives rise to β -bromophthalic acid.

1-Chloro- α -naphthafuran, $C_{12}H_7OCl$, melts at 47° . The corresponding 1-bromo- α -naphthafuran, $C_{12}H_7OBr$, melts at 76° , and 1:8-dibromo- α -naphthafuran, $C_{12}H_6OBr_2$, crystallises from alcohol in lustrous white needles, melting at 109° .

Acetylcoumarone (Abstr., 1897, i, 528) combines with bromine, yielding the bromide, $C_8H_5O \cdot CO \cdot CH_2Br$, which melts at 89° ; when this is heated with the sodium derivative of salicylaldehyde, dicoumaryl ketone, $CO(C_8H_5O)_2$, is produced, and crystallises from alcohol in golden-yellow leaflets melting at 154° .

[With M. HELBIG.]—4-Bromo-1-acetylcoumarone, $C_6H_3Br \begin{smallmatrix} \text{O} \\ \diagup \text{CH} \diagdown \end{smallmatrix} \text{CAc}$, prepared from bromosalicylaldehyde and chloroacetone, crystallises in white needles and melts at 109 – 110° ; the phenylhydrazone, oxime, and semicarbazone melt at 164° , 161° , and 218° , respectively. 4-Chloro-1-acetylcoumarone, $C_6H_3Cl \begin{smallmatrix} \text{O} \\ \diagup \text{CH} \diagdown \end{smallmatrix} \text{CAc}$, melts at 104° ; the oxime and phenylhydrazone melt at 162 – 164° and 90 – 92° respectively.

[With A. TEUDELOFF.]—4-Methoxycoumarone, $OMe \cdot C_6H_3 \begin{smallmatrix} \text{O} \\ \diagup \text{CH} \diagdown \end{smallmatrix} \text{CH}$, obtained from methylacetalylquinol, has a sweet, penetrating odour and boils at 230 – 240° . Methylacetalylquinol,



is a colourless oil which boils at 192 – 194° under 38 mm. pressure, and the aldehyde hydrate, $OMe \cdot C_6H_4 \cdot O \cdot CH_2 \cdot CH(OH)_2$, forms silvery scales which melt at 75 – 76° .

5-Methoxycoumarone, $OMe \cdot C_6H_3 \begin{smallmatrix} \text{O} \\ \diagup \text{CH} \diagdown \end{smallmatrix} \text{CH}$, boils at 232 – 233° , has a sp. gr. 1.1567 at 16° , and refractive index 1.5664 at 18° ; concentrated sulphuric acid develops an intense violet coloration. The picrate melts at 64 – 65° . Will and Beck (Abstr., 1886, 880) obtained the same coumarone from the methyl ether of umbelliferone, but their statement that it boils at 178 – 180° must be incorrect. Methylacetalylresorcinol, $OMe \cdot C_6H_4 \cdot O \cdot CH_2 \cdot CH(OEt)_2$, boils at 170 – 172° under 15 mm. pressure.

[With K. P. GRÄLERT.]—Whilst coumarone and its chloro-derivative are merely resinified by the action of concentrated hydrochloric acid, excess of alcoholic potash at 180 – 190° gives rise to *o*-hydroxyphenylacetic acid. This compound melts at 144 – 145° , and crystallises from turpentine in beautiful needles; the barium salt contains $4H_2O$, and

the *ethyl ether* melts at 103—104°. The lactone, $C_6H_4 \begin{smallmatrix} O \\ \diagup \quad \diagdown \\ CH_2 \end{smallmatrix} CO$, described by Baeyer and Fritsch (Abstr., 1884, 1021), occurs in two modifications, which melt at 28·5° and 49° respectively; phosphorus oxychloride at 120° converts it into 1-chlorocoumarone which boils at 203°. The *amide* of *o*-hydroxyphenylacetic acid melts at 116—117°, and the *anilide* at 151—152°; the *hydrazide* and *phenylhydrazide* melt at 153—154° and 180° respectively. When the lactone is treated with phosphorus pentachloride, the chloride, $C_6H_4 \begin{smallmatrix} O \\ \diagup \quad \diagdown \\ CCl_2 \end{smallmatrix} CH_2$, is produced; elimination of hydrogen chloride from this compound gives rise to 2-chlorocoumarone, which boils at 199—201°. Other products of the action of alcoholic potash on coumarone are coumaranone, and 1- and 2-ethoxycoumarones. Alcoholic potash resolves the dichlorocoumarone which melts at 72° into 5-chloro-2-hydroxyphenylacetic acid, $OH \cdot C_6H_3Cl \cdot CH_2 \cdot CO_2H$, which crystallises from water in slender needles, and melts at 129·5°, the *lactone* melts at 23°.

2-Hydroxy-1-naphthylacetic acid, $OH \cdot C_{10}H_6 \cdot CH_2 \cdot CO_2H$, prepared by heating chloro- β -naphthafuran with alcoholic potash at 180°, crystallises from dilute alcohol in lustrous, white leaflets, and melts at 147°; the *barium*, *calcium*, and *copper* salts are not characteristic. The *lactone*, $C_{10}H_6 \begin{smallmatrix} O \\ \diagup \quad \diagdown \\ CH_2 \end{smallmatrix} CO$, crystallises from alcohol in aggregates of small needles and melts at 104°.

Bromo-2-hydroxynaphthyl-1-acetic acid, $OH \cdot C_{10}H_5Br \cdot CH_2 \cdot CO_2H$, obtained from dibromonaphthafuran and alcoholic potash, crystallises in lustrous needles and melts at 166°; the *lactone*, $C_{10}H_5Br \begin{smallmatrix} O \\ \diagup \quad \diagdown \\ CH_2 \end{smallmatrix} CO$, melts at 97° and boils at 310° under 30 mm. pressure. Sodium amalgam reduces the acid to 2-hydroxynaphthylacetic acid, melting at 147°, and alkaline potassium permanganate oxidises it to β -bromophthalic acid. Trichloro- β -naphthafuran yields dichlorohydroxynaphthylacetic acid, $C_{12}H_8O_3Cl_2$, when heated with alcoholic potash; this acid crystallises in lustrous leaflets and melts at 194°.

o-Hydroxymandelic aldehyde, $OH \cdot C_6H_4 \cdot CH(OH) \cdot CHO$, obtained on heating coumarone dichloride with aqueous sodium acetate at 40—50° while the liquid is vigorously agitated, crystallises from water in long, white needles melting at 63—64°; ferric chloride develops a deep reddish-violet coloration, and sodium hydroxide dissolves the aldehyde, forming a yellow solution. The *semicarbazone* melts at 189—190°, and the *osazone* crystallises from alcohol and melts at 197°.

M. O. F.

Indene, and Coumarone Resins. By GUSTAV KRAEMER and ADOLF SPILKER (*Ber.*, 1900, 33, 2257—2264).—When a solution of coumarone in benzene is shaken with sulphuric acid, the greater part is converted into a resin soluble in benzene, whilst the remainder separates as a brown powder. If 80 per cent. sulphuric acid is employed, the soluble resin is almost exclusively obtained, but the yield of the insoluble resin increases with the concentration of the acid, until, with

95 per cent. acid, the coumarone is precipitated in the latter form nearly quantitatively. The pure soluble resin melts at 107—108°, and has a sp. gr. 1.25 at 19°; its composition, C_9H_6O , is identical with that of coumarone, but its molecular weight is four times as great. When this resin is heated at 300—350°, a distillate is obtained consisting mainly of coumarone, together with some phenol, ethylbenzene, and small quantities of *o*-ethylphenol, benzene, toluene, and hydrocoumarone.

By the action of sulphuric acid (75 per cent.) on indene, it is converted into a resin which is soluble in benzene; this resin has the same composition as indene itself, but a variable melting point and molecular weight. The white resin obtained in this way melts at 210°. Under certain conditions, a compound of indene with sulphuric acid can be isolated; its barium salt, $(C_9H_9 \cdot OSO_3)_2Ba$, forms yellow, indistinctly crystalline plates. The indene resin decomposes at 290—340°, yielding a distillate which consists of indene, together with some hydrindene and phenol.

The polymerisation of coumarone proceeds with very little rise of temperature, whilst that of indene produces considerable development of heat; in both cases, it can also be effected by means of aluminium chloride.

If crude, heavy benzene, boiling at 155—185°, is treated with sulphuric acid and the resulting mixture of resins distilled, a fraction is obtained at 168—172° which consists of coumarone and hydrindene; the coumarone may be separated as the picrate, and can be more easily obtained in this manner than directly from the heavy benzene. The greater part of the indene, however, is decomposed. E. G.

Esterification of Unsymmetrical Polybasic Acids. I. Esterification of Nitroterephthalic Acid. By RUDOLF WEGSCHEIDER (*Monatsh.*, 1900, 21, 621—637. Compare *Abstr.*, 1895, ii, 310; 1898, i, 30 and 238).—Good yields of nitroterephthalic acid may be obtained by Burkhardt's method (*Ber.*, 1877, 10, 145), even when as much as 20 grams of terephthalic acid are employed in one operation. The nitro-acid melts at 259.5° (corr.) and the normal methyl ester at 74—75°. The acid potassium salt, $C_8H_4O_6NK \cdot H_2O$, silver salt, $C_8H_3O_6Na_2$, and lead salt, $C_8H_3O_6NPb \cdot 3H_2O$, have been prepared. The normal methyl ester is obtained by the action of methyl iodide on the acid potassium salt, or of methyl alcohol on the acid alone or in presence of hydrochloric or sulphuric acid. It crystallises in triclinic prisms [$a:b:c = 1.4745:1:0.52248$; $a = 100^\circ 51.6'$, $\beta = 98^\circ 10.2'$, $\gamma = 107^\circ 14.8'$].

The normal *n*-propyl ester is a colourless, mobile liquid distilling at 228—230° (corr.) under 18 mm. pressure, and does not solidify at 0°. When benzyl alcohol and nitroterephthalic acid are heated together, benzaldehyde and benzyl aminoterephthalate are formed; the latter crystallises in needles melting at 99—101°, and forms a hydrochloride which is insoluble in ether. When the alcohol and acid are heated in the presence of sulphuric acids, the products are benzyl ether, and probably azo- and amino-terephthalic acids. The acid is also reduced to the amino-acid when heated with menthol. J. J. S.

Esterification of Unsymmetrical Polybasic Acids. II. Esterification of Bromo- and Hydroxy-terephthalic Acids. By RUDOLF WEGSCHEIDER and KARL BITTNER (*Monatsh.*, 1900, 21, 638—654. Compare preceding abstract).—Bromoterephthalic acid has been obtained by Sandmeyer's method from the amino-acid and hydroxyterephthalic acid by Burkhardt's method (*Ber.*, 1877, 10, 145). When the acid potassium salts of the two acids are treated with methyl iodide, α -acid esters are formed, and the rule previously enunciated is followed. By the esterification of the bromo-acid, normal and β -acid esters are formed; with the hydroxy-acid, the normal ester alone is produced when hydrochloric acid or much sulphuric acid is employed, but with only a small amount of sulphuric acid the β -acid ester is also obtained. When the normal ester of the bromo-acid is hydrolysed by alkali, the α -acid ester is formed, but from the normal ester of the hydroxy-acid the β -acid ester is obtained.

In the esterification, the same acid ester is obtained, whether the catalytic or autocatalytic method is employed. Methyl bromoterephthalate, $C_6H_3Br(CO_2Me)_2$, melts at 54° ; both α - [$CO_2H : Br : CO_2Me = 1 : 2 : 4$] and β - [$CO_2Me : Br : CO_2H = 1 : 2 : 4$] *methyl hydrogen terephthalate* crystallise in glistening needles from their aqueous solutions, dissolve readily in most organic solvents, the α -compound is somewhat more sparingly soluble in cold water than the β -, and its neutral solution gives a precipitate with lead acetate which is soluble in excess and not reprecipitated on boiling; the β -compound behaves similarly, except that the precipitate is thrown down again on boiling. Slight differences with copper sulphate and silver nitrate solutions are also observable. The constitutions of the two compounds follow from their electrical conductivities (compare Wegscheider, *Abstr.*, 1895, ii, 310). α -Methyl hydrogen terephthalate melts at 145° and has the dissociation constant K 0.037; the β -acid ester melts at 164° and has K 0.50.

α -Methyl hydrogen hydroxyterephthalate, [$CO_2Me : OH : CO_2H = 1 : 2 : 4$], crystallises in needles, melts at 206 — 208° , is readily soluble in ether, alcohol, or warm benzene, but is not so readily soluble in chloroform as the isomeride, and gives a reddish-yellow colour with ferric chloride.

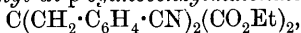
β -Methyl hydrogen hydroxyterephthalate [$CO_2H : OH : CO_2Me = 1 : 2 : 4$] melts at 177° , and gives a purple colour with ferric chloride.

J. J. S.

***p*-Cyanobenzyl Chloride.** By NATHAN MOSES (*Ber.*, 1900, 33, 2623—2630. Compare Mellinshoff, *Abstr.*, 1890, 239; Günther, *ibid.*, 977; Reinglass, 1891, 1344; and Banse, 1894, i, 574).—The reactions between various reagents and *p*-cyanobenzyl chloride have been studied, and the products isolated. *p*-Cyanobenzyl thiocyanate, $CN \cdot C_6H_4 \cdot CH_2 \cdot SCN$, forms glistening needles melting at 85 — 86° , and when heated with concentrated hydrochloric acid at 180° yields benzylsulphide-*p*-dicarboxylic acid, $S(CH_2 \cdot C_6H_4 \cdot CO_2H)_2$, the nitrile of which, obtained by the action of potassium hydrogen sulphide on *p*-cyanobenzyl chloride, crystallises in yellowish plates melting at 114.5° . A good yield of *p*-cyanocinnamic acid melting at 248 — 249° is obtained when *p*-cyanobenzaldehyde, potassium acetate and acetic acid are heated, but when sodium acetate is employed a small amount

of a substance melting at 165° , and probably *p*-aldehydobenzamide is the only product. *p*-Cyanophenylpropionic acid crystallises in six-sided prisms melting at 135 – 136° , and on hydrolysis yields the dibasic acid, $\text{CO}_2\text{H}\cdot\text{C}_6\text{H}_4\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{CO}_2\text{H}$, which decomposes at 280° . Ethyl di-*p*-cyanobenzylacetoacetate, $\text{CAc}(\text{CH}_2\cdot\text{C}_6\text{H}_4\cdot\text{CN})_2\cdot\text{CO}_2\text{Et}$, crystallises in needles melting at 133 – 134° .

Ethyl di-*p*-cyanobenzylcyanoacetate, $\text{CN}\cdot\text{C}(\text{CH}_2\cdot\text{C}_6\text{H}_4\cdot\text{CN})_2\cdot\text{CO}_2\text{Et}$, obtained from ethyl sodiocyanoacetate, melts at 110.5° , and on hydrolysis yields di-*p*-carboxybenzylacetic acid, $\text{CO}_2\text{H}\cdot\text{CH}(\text{CH}_2\cdot\text{C}_6\text{H}_4\cdot\text{CO}_2\text{H})_2$, melting at 270 – 271° . Ethyl di-*p*-cyanobenzylmalonate,



melts at 194° , and when hydrolysed yields the tribasic acid melting at 270 – 271° . *p*-Cyanodiphenylmethane, obtained from *p*-cyanobenzyl chloride, benzene, and aluminium chloride, crystallises in prisms melting at 50 – 51° , and on hydrolysis gives diphenylmethane-*p*-carboxylic acid, $\text{CH}_2\text{Ph}\cdot\text{C}_6\text{H}_4\cdot\text{CO}_2\text{H}$, melting at 157 – 158° . *p*-Cyanophenyltolylmethane is an oil distilling at 198 – 199° under 15 mm. pressure. Phenyltolylmethane-*p*-carboxylic acid, $\text{C}_6\text{H}_4\text{Me}\cdot\text{CH}_2\cdot\text{C}_6\text{H}_4\cdot\text{CO}_2\text{H}$, crystallises in colourless needles melting at 134 – 135° .

Di-*p*-cyanodibenzylamine, $\text{NH}(\text{CH}_2\cdot\text{C}_6\text{H}_4\cdot\text{CN})_2$, obtained by shaking *p*-cyanobenzyl chloride with 10 per cent. alcoholic ammonia, crystallises in prisms melting at 105 – 106° , and on hydrolysis with hydrochloric acid yields di-*p*-carboxydibenzylamine hydrochloride, which melts above 280° . Tri-*p*-cyanotribenzylamine hydrochloride, $\text{N}(\text{CH}_2\cdot\text{C}_6\text{H}_4\cdot\text{CN})_3\cdot\text{HCl}$, crystallises in acicular groups decomposing between 270° and 280° .

O. Fischer's *p*-cyanotriphenylmethane may be obtained from cyanobenzylidene chloride, benzene, and aluminium chloride. J. J. S.

Transformation of Coloured Unsaturated Dicarboxylic Acids into Colourless Stereoisomerides. By HANS STOBBE (*Chem. Centr.*, 1900, ii, 561–562; from *Verh. Ver. Deutsch. Naturf. Aerzte*, 1899, 88–90).—Dibenzylidenesuccinic acid, $\text{C}_2(\text{:CHPh})_2(\text{CO}_2\text{H})_2$, prepared by the action of sodium ethoxide, free from alcohol, on an ethereal solution of benzaldehyde (2 mols.) and ethyl succinate (1 mol.), melts at 218° ; on oxidation, it yields benzaldehyde and oxalic acid, and on reduction dibenzylsuccinic acid, $\text{C}_{18}\text{H}_{18}\text{O}_4$. Dibenzylidenesuccinic anhydride is a lemon-yellow substance, which melts at 203 – 204° , and when treated with resorcinol forms a compound analogous to fluorescein which by the action of bromine yields an eosin. By exposing solutions of the anhydride in benzene containing iodine to the action of sunlight, the stereoisomerides of dibenzylidenesuccinic acid are obtained in the form of their anhydrides. isoDibenzylidenesuccinic anhydride separates in granules and melts at 254 – 255° . alloDibenzylidenesuccinic anhydride forms small scales and melts at 223° . Both are colourless substances and very sparingly soluble in benzene. In one case an anhydride melting at 172 – 175° was obtained, but by the further action of light it was converted into the isoanhydride. The acids corresponding with the anhydrides are also colourless compounds. isoDibenzylidenesuccinic acid loses water before it melts; allodibenzylidenesuccinic acid melts at 203 – 210° and decomposes at 220° .

Acids of similar constitution are formed by condensing γ -disubstituted ethyl itaconate with aldehydes and ketones in presence of sodium ethoxide. γ -Diphenyl- α -benzylideneitaconic acid, $C_{24}H_{18}O_4$, prepared from benzaldehyde and ethyl diphenylitaconate, is a yellow substance and melts and decomposes at $218-219^\circ$. By exposing benzene solutions of the acid or of the red anhydride containing iodine to the action of sunlight, a heavy, colourless acid and a heavy, colourless anhydride are formed respectively; the latter melts at 267° . A third colourless isomeride melting at 247° is also formed.

From these experiments it is evident that the colour of all these compounds may stand in some fixed relationship to their configuration in space.

E. W. W.

Coloured Sulphur Compounds of the Diphenyl- and Triphenyl-methane series. I. By RICHARD E. MEYER (*Ber.*, 1900, **33**, 2570—2576).—By fusion with sodium sulphide, fluorescein is converted into 1-thiofluorescein, in which the oxygen of the pyrone ring is replaced by sulphur, whereas fluoran, in which no hydroxyl groups are present, does not react in this way. On the other hand, by the action of phosphorus pentasulphide, the carbonyl and lactone oxygen of fluoran, diphenylphthalide, xanthone, and thioxanthone, are readily replaced by sulphur, whilst this reaction only occurs very imperfectly or not at all with fluorescein and similar derivatives. No definite relation could be established between the degree of fluorescence of the compound and the number and position of the sulphur atoms present, and similar irregularities are presented by the melting points of these compounds. The thiolactones and thioketones yielded by colourless ketones and lactones are strongly coloured, and this affords additional evidence of the marked chromophoric function of the sulphur atom.

The experimental details are given in the following abstract.

A. H.

Coloured Sulphur Compounds of the Diphenyl- and Triphenyl-methane Series. II. By RICHARD E. MEYER and J. SZANECKI (*Ber.*, 1900, **33**, 2577—2584. Compare preceding abstract).

—*Dithiofluoran*, $CS\langle\begin{smallmatrix} C_6H_4 \\ S \end{smallmatrix}\rangle C\langle\begin{smallmatrix} C_6H_4 \\ C_6H_4 \end{smallmatrix}\rangle O$, is formed when fluoran is heated with phosphorus pentasulphide, and crystallises in thick red needles, melting at $155-156^\circ$. Alcoholic soda reconverts it into fluoran, and on distillation with lime it yields xanthone, so that the sulphur atoms must be situated in the lactone ring. In sulphuric acid solution, it shows a very faint green fluorescence. *Dithiofluorescein chloride* (*dichlorodithiofluoran*), $CS\langle\begin{smallmatrix} C_6H_4 \\ S \end{smallmatrix}\rangle C\langle\begin{smallmatrix} C_6H_3Cl \\ C_6H_3Cl \end{smallmatrix}\rangle O$, is formed by the action of phosphorus pentasulphide on fluorescein chloride, and crystallises in light red needles melting at $196-197^\circ$. Diphenylphthalide also reacts with phosphorus pentasulphide, yielding *dithiodiphenylphthalide*, $CS\langle\begin{smallmatrix} C_6H_4 \\ S \end{smallmatrix}\rangle CPh_2$, which forms brick-red prisms melting at $161-162^\circ$. Xanthone is converted by the same reagent into xanthione, $CS\langle\begin{smallmatrix} C_6H_4 \\ C_6H_4 \end{smallmatrix}\rangle O$ (Graebe and Roeder, *Abstr.*, 1899,

i, 705), whilst thioxanthone yields *dithioxanthone* (thioxanthione), $\text{CS} \langle \text{C}_6\text{H}_4 \rangle \text{S}$, which is a yellow powder and melts and decomposes at 215° . The solution in sulphuric acid has a reddish-brown colour, and possesses a distinct yellow fluorescence.

Thiofluorescein has been already described by Wyler (*Diss.*, Zurich, 1894); it dissolves in alkalis, forming a rose-pink solution with a faint green fluorescence. Phosphorus pentabromide converts it into *thiofluorescein bromide*, $\text{CO} \langle \text{C}_6\text{H}_4 \rangle \text{C} \langle \text{C}_6\text{H}_3\text{Br} \rangle \text{S}$, which is a brown powder melting at 252° . A. H.

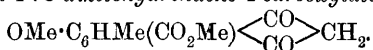
Mixed Esters of Cochinelic Acid. By JOSEF LANDAU (*Ber.* 1900, 33, 2442—2446).—When cochinelic acid (compare Liebermann and Voswinckel, *Abstr.*, 1897, i. 539) in ammoniacal solution is precipitated with lead acetate, a *dilead* salt, $\text{C}_{10}\text{H}_4\text{O}_7\text{Pb}_2$, is obtained. This, however, reacts with methyl iodide just as the trisilver salt does.

When dry trisilver cochinelate is heated with excess of methyl iodide at 100° , a mixture of the *methyl ethers* of *trimethyl* and *dimethyl hydrogen cochinelate*,

$\text{OMe} \cdot \text{C}_6\text{HMe}(\text{CO}_2\text{Me})_3$ and $\text{OMe} \cdot \text{C}_6\text{HMe}(\text{CO}_2\text{H})(\text{CO}_2\text{Me})_2$, is obtained; these can be separated by means of aqueous sodium carbonate. The yield of trimethyl ester is comparatively small; it can be increased greatly by using, instead of the pure silver salt, a mixture of it with silver oxide, obtained by precipitating with silver nitrate a solution of 1 mol. of cochinelic acid in 4 mols. of aqueous potassium hydroxide. The trimethyl ester melts at 111 — 113° , the dimethyl ester at 58 — 62° when dried in the air, at 85 — 87° when dried in a vacuum desiccator, in which it effloresces; neither ester gives a colour reaction with ferric chloride. When the dimethyl ester (1 mol.), best mixed with silver oxide in excess, is heated at 100° with methyl alcoholic potassium methoxide (1 mol.) and methyl iodide, it is converted into the trimethyl ester. When these esters are treated either with 5 per cent. aqueous barium hydroxide or with 25 per cent. aqueous potassium hydroxide, the methoxyl group is hydrolysed as well as the carbomethoxyl groups, and cochinelic acid is obtained at once. The unusually ready passage from the OH to the OMe group, and *vice versa*, is noteworthy. C. F. B.

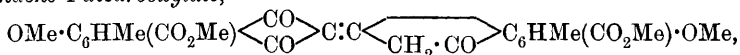
Diketohydrindene Derivatives of Cochinelic Acid. By JOSEF LANDAU (*Ber.*, 1900, 33, 2446—2453).—When trimethylcochinelate methyl ether, $\text{OMe} \cdot \text{C}_6\text{HMe}(\text{CO}_2\text{Me})_3$ (preceding abstract), is heated at 100° with metallic sodium, and methyl acetate is added gradually, a yellow *sodium* derivative, $\text{C}_{15}\text{H}_{13}\text{O}_7\text{Na}$, which crystallises with $1\text{H}_2\text{O}$, is formed. When an aqueous solution of this salt is acidified, the sodium is removed and *dimethyl 5-methoxy-7-methyl-1:3-diketohydrindene-2:4-dicarboxylate*, $\text{OMe} \cdot \text{C}_6\text{HMe}(\text{CO}_2\text{Me}) \langle \text{CO} \rangle \text{CH} \cdot \text{CO}_2\text{Me}$, is precipitated. This forms an orange-yellow powder which melts and decomposes at 98 — 100° , and gives a reddish-brown coloration with ferric

chloride; in ethereal solution it decomposes gradually, forming *methyl 5-methoxy-7-methyl-1:3-diketohydrindene-4-carboxylate*,



This melts and decomposes at 160—161°; it dissolves in alkalis; when heated with protocatechualdehyde at 150°, it condenses to *methyl 2-m-p-dihydroxybenzylidene-5-methoxy-7-methyl-1:3-diketohydrindene-4-carboxylate*, $\text{OMe} \cdot \text{C}_6\text{HMe}(\text{CO}_2\text{Me}) \begin{array}{c} \diagup \text{CO} \diagdown \\ \diagdown \text{CO} \diagup \end{array} \text{C} : \text{CH} \cdot \text{C}_6\text{H}_3(\text{OH})_2$, which is brownish-yellow, melts at 264—266°, dyes mordants, and dissolves in alkalis.

When the yellow sodium derivative is heated with fuming hydrochloric acid at 100°, *dimethyl anhydrobis-5-methoxy-7-methyldiketohydrindene-4-dicarboxylate*,



is produced. This forms yellow crystals, melts at 243—244°, dissolves in alkalis, and does not dye mordants; when heated with methyl alcoholic potassium methoxide at 100°, it yields the *acid* or the *methyl hydrogen* ester, according as the alkali is used in excess or not; attempts to hydrolyse the methoxyl groups were unsuccessful. The methyl hydrogen ester melts at 222—223°, the acid melts and decomposes at 294—296°; both form yellow crystals, dissolve in alkalis, and give coloured precipitates with salts of heavy metals. C. F. B.

Constitution of Usnic Acid. By EMANUELE PATERNO (*Atti. Real. Accad. Lincei*, 1900, [v], 9, ii, 119—132. Compare Widman, this vol., i, 235, 347).—An historical account is given of the chemistry of usnic acid, the results of Widman (*loc. cit.*) and of Hesse being criticised. The following are the new results obtained by the author.

Benzoylusnic acid, $\text{C}_{18}\text{H}_{16}\text{O}_7 \cdot \text{Bz}$ or $\text{C}_{18}\text{H}_{16}\text{O}_8\text{Bz}$, obtained by heating a dilute potassium hydroxide solution of the acid with benzoyl chloride, separates from alcohol, ethyl acetate, or benzene in lustrous, orange-yellow, monoclinic prisms melting at 218—220°. [$a:b:c = 1.9458:1:0.9340$; $\beta = 56^\circ 25' 30''$]. The *oxime*, $\text{C}_{18}\text{H}_{15}\text{O}_6\text{N}$, melts at 226—228°, and is soluble in alcohol or acetic acid. By the action of phenylhydrazine on the acid in acetic acid solution, a *phenylhydrazone* of an anhydro-acid of the composition $\text{C}_{24}\text{H}_{22}\text{O}_6\text{N}_2$ or $\text{C}_{24}\text{H}_{20}\text{O}_5\text{N}_2$ is obtained, melting at 194—195°; it does not yield usnic acid on treatment with acetic and sulphuric acids, as was the case with the compound prepared by Widman (*loc. cit.*). On heating decarbusnein with sodium acetate and acetic anhydride, the diacetyl derivative of decarbusnic acid is formed, from which it is concluded that the molecule of usnic acid contains an acetyl radicle. Usnic acid, prepared by heating usnic acid with sulphuric acid, may also be obtained by treating decarbusnein in the same way. The basicity of usnic and decarbusnic acids is discussed, the constitutions given by Widman being regarded as erroneous; Widman's observation that usnic acid is optically active is confirmed. T. H. P.

Oxidation with Atmospheric Oxygen. By HEINRICH BILTZ (*Ber.*, 1900, 33, 2295—2299).—When a stream of air is passed through

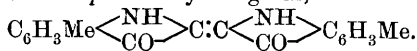
a solution of dibromo-*p*-hydroxybenzaldehyde, phenylhydrazone and potassium hydroxide, *tetrabromodihydroxybenzilozone*, $C_{25}H_{20}O_2N_4Br_4$, is obtained as a crystalline powder; it melts at 206° , and dissolves in warm acetic acid or alcohol, but is only sparingly soluble in light petroleum, chloroform, benzene, or water. An equivalent quantity of hydrogen peroxide is simultaneously produced. E. G.

Halogenised Aromatic Amino-ketones. By FRANZ KUNCKELL (*Ber.*, 1900, 33, 2644—2654).—[With G. TREUTLER].—*p*-Chloroacetylacetanilide, $CH_2Cl \cdot CO \cdot C_6H_4 \cdot NHAc$, made by the action of aluminium chloride on a mixture of acetanilide and chloroacetyl chloride (compare following abstract), crystallises from a mixture of chloroform and alcohol in small, white needles, is sparingly soluble in alcohol or water, but readily in chloroform, and melts at 212° . It yields *p*-acetylaminobenzoic acid when oxidised with potassium permanganate. *p*-Chloroacetylaniline, $CH_2Cl \cdot CO \cdot C_6H_4 \cdot NH_2$, crystallises in yellow or reddish-yellow leaflets, melts at 147° , and dissolves readily in alcohol and less readily in ether or benzene.

p-Acetylaminobenzoylmethyl acetate, $CH_3 \cdot CO_2 \cdot CH_2 \cdot CO \cdot C_6H_4 \cdot NHAc$, made by heating *p*-chloroacetylaniline dissolved in alcohol with potassium acetate, crystallises from water in small, white needles melting at 162° . The corresponding benzoate, $C_6H_5 \cdot CO_2 \cdot CH_2 \cdot CO \cdot C_6H_4 \cdot NHAc$, forms white, felted needles and melts at 200 — 201° . *p*-Aminobenzoylmethyl acetate crystallises from benzene in white needles and melts at 135° .

p-Acetylaminobenzoylcarbinol, $OH \cdot CH_2 \cdot CO \cdot C_6H_4 \cdot NHAc$, obtained by shaking the acetate with 15 per cent. sodium hydroxide solution, crystallises in white leaflets, melts at 176 — 177° , and dissolves readily in chloroform and alcohol, but is nearly insoluble in ether or benzene. The phenylhydrazone, $C_{16}H_{17}O_2N_3$, separates from alcohol in yellow needles melting at 223° . *p*-Aminobenzoylcarbinol crystallises from benzene in bright yellow needles melting at 165° , and is soluble in alcohol or in acids, but only very sparingly in water. The hydrochloride, $C_8H_9O_2N \cdot HCl$, melts above 250° , and the phenylhydrazone, $C_{14}H_{15}ON_3$, crystallises in yellow needles and melts at 199° .

When aceto-*p*-toluidide is treated with chloroacetic chloride, both the chloroacetyl-*o*- and *m*-toluidines are obtained. Chloroacetylaceto-*p*-toluidide, $CH_2Cl \cdot CO \cdot C_6H_3Me \cdot NHAc$, separates from alcohol in white needles melting at 180 — 181° , and dissolves readily in alcohol, ether, chloroform, benzene, or light petroleum; when warmed with potassium hydroxide solution, it is, as a result of hydrolysis and oxidation, partially converted into *p*-dimethylindigotin,

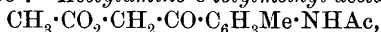


Chloroacetyl-*p*-toluidine melts at 136° .

Chloroacetylaceto-*m*-toluidide crystallises from dilute alcohol in yellow, cube-like crystals melting at 120° , dissolves readily in alcohol, chloroform, or benzene, and sparingly in ether or light petroleum. Chloroacetyl-*m*-toluidine, $CH_2Cl \cdot CO \cdot C_6H_3Me \cdot NH_2$, melts at 75° .

[With G. HECKER].—Chloroacetyl-*o*-toluidine, from aceto-*o*-toluidide,

crystallises from alcohol in slender, white needles and melts at 160° ; when warmed with strong aqueous potash, it is not oxidised to an indigo derivative, so that the chloroacetyl group is not in the ortho-position with regard to the acetylamino-group; it is oxidised by permanganate to a dicarboxylic acid, $C_{10}H_9O_5N$, of unknown constitution; on nitration, it yields a *mononitro*-derivative, $C_{11}H_{11}O_4N_2Cl$, which melts at 205° . *Acetylamino-o-tolylmethyl acetate*,



crystallises from alcohol in white needles and melts at 90° ; the corresponding *benzoate*, $C_{18}H_{17}O_4N$, forms white needles and melts at 130° . *Chloroacetyl-o-toluidine*, $CH_2Cl \cdot CO \cdot C_6H_3Me \cdot NH_2$, separates from alcohol in white leaflets melting at 75° ; the *hydrochloride*, $C_9H_{11}ONCl_2$, decomposes at about 170° .

Chloroacetyl-as-aceto-m-xylylidide, $C_{12}H_{14}O_2NCl$, crystallises from alcohol, in which it is readily soluble, in long, white needles melting at 150° . *Chloroacetyl-as-m-xylylidine*, $CH_2Cl \cdot CO \cdot C_6H_3Me_2 \cdot NH_2$, melts at 126° ; its *hydrochloride* forms long, white needles which decompose without melting at 150° . *Chloroacetylnitroxylidene*, $C_{12}H_{13}O_4N_2Cl$, crystallises from alcohol and melts at 202° .

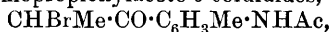
p-Amino-m-dimethylbenzoylmethyl acetate, $C_{12}H_{15}O_3N$, from *chloroacetyl-as-m-xylylidine*, crystallises in yellowish leaflets melting at 109° , and the corresponding *benzoate* forms needles melting at $118-119^{\circ}$. The free carbinol could not be obtained.

Chloroacetylaceto-ψ-cumidide, $CH_2Cl \cdot CO \cdot C_6HMe_3 \cdot NHAc$



crystallises from dilute alcohol in white needles melting at 189° . *Chloroacetyl-ψ-cumidine*, $CH_2Cl \cdot CO \cdot C_6HMe_3 \cdot NH_2$, crystallises from water in pearly leaflets and melts at 70° ; the *hydrochloride* forms white needles melting at 245° . *Chloroacetylnitroaceto-ψ-cumidide*, $C_{13}H_{15}O_4N_2Cl$, crystallises from alcohol in white, felted needles and melts at 200° .

Two isomeric bromopropionylaceto-o-toluidides,



were obtained by treating a mixture of aceto-o-toluidide and bromopropionyl bromide with aluminium chloride in direct sunlight; the one forms bundles of white needles melting at 158° , and the other small, white needles melting at 138° .

α-Bromopropionylacetoxylidide, $C_{13}H_{16}O_2NBr$, crystallises from alcohol in white leaflets melting at $115-116^{\circ}$.

α-Bromopropionylaceto-ψ-cumidide, $C_{14}H_{18}O_2NBr$, separates from dilute alcohol in a crystalline condition and melts at 146° . A. L.

New Method of Preparing Aromatic Amino-ketones. By FRANZ KUNCKELL (*Ber.*, 1900, 33, 2641—2644).—A good general method of preparing aromatic amino-ketones consists in allowing aluminium chloride to act on a mixture of acetanilide and an acyl chloride, carbon disulphide being used as a diluent. The resulting acetyl compounds are afterwards hydrolysed by boiling with 15 per cent. hydrochloric acid.

p-Propionylacetanilide, $COEt \cdot C_6H_4 \cdot NHAc$, crystallises from water

in yellow needles melting at 161° . *p*-Propionylaniline is soluble in water and alcohol, crystallises in long, yellow needles, and melts at 140° ; the *hydrochloride* and *sulphate* form white crystals and melt at 198° and 225° respectively.

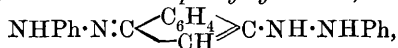
p-n-Butyrylacetanilide, $\text{COPr}^{\alpha}\cdot\text{C}_6\text{H}_4\cdot\text{NHAc}$, crystallises in white needles and melts at 142° . *p*-n-Butyrylaniline dissolves readily in alcohol and water and melts at 84° ; the *hydrochloride* melts at 178° , and the *sulphate* at 216° .

Ethyl p-propionylphenylcarbamate, $\text{COEt}\cdot\text{C}_6\text{H}_4\cdot\text{NH}\cdot\text{CO}_2\text{Et}$, crystallises in white needles and melts at 154° . *p*-Propionylphenylcarbamide, $\text{COEt}\cdot\text{C}_6\text{H}_4\cdot\text{NH}\cdot\text{CO}\cdot\text{NH}_2$, melts at 218° . A. L.

New Synthesis of Ketones. By EDGAR WEDEKIND (*Chem. Centr.*, 1900, ii, 561; from *Verh. Ver. Deutsch. Naturf. Aerzte*, 1899, 108—110).—By the action of phenylacetyl chloride on triethylamine dissolved in anhydrous ether or benzene, triethylamine hydrochloride and a compound, $(\text{CHPh}\cdot\text{CO})_x$, are formed, no intermediate additive compound being produced. The crude product is a thick oil, and on distillation under 8—10 mm. pressure yields a clear, yellow oil from which a crystalline oxime may be prepared. The ketone obtained from the oxime yields a phenylhydrazone identical with that formed by the action of phenylhydrazine on the crude oil. From the crude product, however, a ketone of a different constitution has been isolated; it is a crystalline substance and melts at 170 — 171° . The formation of dehydracetic acid by the action of acetyl chloride on triethylamine is probably due to the polymerisation of a ketone. Since many acid haloids also form primary products which react with water to form corresponding acid anhydrides, this action may possibly constitute a new method of preparing ketones. E. W. W.

3-Bromo-1-indone and its Derivatives. By S. SCHLOSSBERG (*Ber.*, 1900, 33, 2425—2432).—3-Bromo-1-indone, $\text{C}_6\text{H}_4\langle\text{CO}\rangle_{\text{CBr}}\text{CH}$, prepared by distilling phenylpropionic acid hydrobromide with phosphoric oxide in a vacuum, forms small, yellow needles and melts at 64° ; bromine converts it into dibromoindone, and strong nitric or sulphuric acid into dibromodiketohydrindene.

3-Anilino-1-indone, $\text{CO}\langle\text{CH}\rangle_{\text{C}_6\text{H}_4}\text{C}\cdot\text{NHPh}$, crystallises from alcohol in bronze-coloured, metallic flakes and melts with decomposition at 204 — 205° . 3-Benzylamino-1-indone, $\text{CO}\langle\text{CH}\rangle_{\text{C}_6\text{H}_4}\text{C}\cdot\text{NH}\cdot\text{CH}_2\text{Ph}$, crystallises from alcohol in orange needles and melts at 153° . These two compounds are converted by fuming hydrochloric acid into diketohydrindene. 3-Bromo-1-indoxime, $\text{CBr}\langle\text{C}_6\text{H}_4\rangle_{\text{CH}}\text{C}\cdot\text{N}\cdot\text{OH}$, crystallises from dilute alcohol in minute, yellow needles and melts at 98° . 3-Phenylhydrazino-1-indonephenylhydrazone,



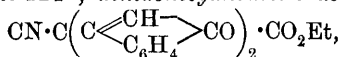
or $\text{NHPh}\cdot\text{N}\cdot\text{C}\langle\text{C}_6\text{H}_4\rangle_{\text{CH}_2}\text{C}\cdot\text{N}\cdot\text{NHPh}$, forms small, reddish-brown

needles and melts and decomposes at 142° . *Diindoneacetic acid*, $\text{CH}(\text{C} \begin{smallmatrix} \text{CH} \\ \text{C}_6\text{H}_4 \end{smallmatrix} \text{CO})_2 \cdot \text{CO}_2\text{H}$, prepared by the action of sodium ethoxide on a mixture of ethyl malonate and bromoindone, crystallises from alcohol in small, yellow needles and melts at 192° ; the sodium salt is orange-coloured, and only slightly soluble in water and alcohol.

Diindoneacetone, $\text{CHAc}(\text{C} \begin{smallmatrix} \text{CH} \\ \text{C}_6\text{H}_4 \end{smallmatrix} \text{CO})_2$, prepared by the action of ethyl sodioacetoacetate on 3-bromoindone, crystallises from alcohol in small, dull yellow needles and melts at 212° .

Diindoneacetophenone, $\text{CHBz}(\text{C} \begin{smallmatrix} \text{CH} \\ \text{C}_6\text{H}_4 \end{smallmatrix} \text{CO})_2$, prepared by the action of ethyl sodiobenzoylacetate on 3-bromoindone, crystallises from alcohol in small, glistening, yellow needles and melts at 246° .

Ethyl indonecyanoacetate, $\text{CO} \begin{smallmatrix} \text{CH} \\ \text{C}_6\text{H}_4 \end{smallmatrix} \text{C} \cdot \text{CH}(\text{CN}) \cdot \text{CO}_2\text{Et}$, prepared by the action of sodium ethoxide on 3-bromoindone and ethyl cyanoacetate in the cold, crystallises from dilute alcohol in small, brown needles and melts at 124° ; *diindonecyanoacetic acid*,



produced when hot solutions are used, crystallises from alcohol in small, glistening, dark yellow needles and melts and decomposes at 285° ; the sodium salt is orange-red and only slightly soluble in water.

Diindonemalonitrile, $\text{C}(\text{CN})_2(\text{C} \begin{smallmatrix} \text{CH} \\ \text{C}_6\text{H}_4 \end{smallmatrix} \text{CO})_2$, crystallises from acetic acid in small, reddish-brown needles and melts with decomposition at 310° . *Diindonebenzoylacetone*, $\text{CAcBz}(\text{C} \begin{smallmatrix} \text{CH} \\ \text{C}_6\text{H}_4 \end{smallmatrix} \text{CO})_2$, crystallises from alcohol in small, yellow needles and melts at 258° .

T. M. L.

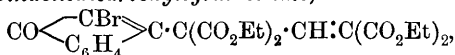
Halogen-substituted Indone Derivatives of β -Diketones. By THEODOR LANSER and FRITZ WIEDERMANN (*Ber.*, 1900, **33**, 2418—2424. Compare Liebermann, *Abstr.*, 1899, i, 373 and 522).—*Chloroindone-*

malononitrile, $\text{CO} \begin{smallmatrix} \text{CCl} \\ \text{C}_6\text{H}_4 \end{smallmatrix} \text{C} \cdot \text{CH}(\text{CN})_2$, crystallises from dilute acetic acid in reddish-brown needles and melts with frothing at 159° .

Chloroindonecyanoacetamide, $\text{CO} \begin{smallmatrix} \text{CCl} \\ \text{C}_6\text{H}_4 \end{smallmatrix} \text{C} \cdot \text{CH}(\text{CN}) \cdot \text{CO} \cdot \text{NH}_2$, crystallises from alcohol in white, but from acetic acid in yellow, needles, and melts at 208 — 209° .

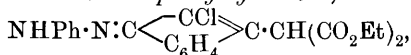
Ethyl bischloroindonemalonate, $\text{C}_2(\text{C} \begin{smallmatrix} \text{CCl} \\ \text{C}_6\text{H}_4 \end{smallmatrix} \text{CO})_2(\text{CO}_2\text{Et})_4$, prepared by the action of moist silver oxide on ethyl chloroindonemalonate, crystallises in minute, white needles and melts at 219 — 220° .

Ethyl bromoindonedicarboxylglutaconate,



crystallises from alcohol in yellow needles and melts at 131° .

Ethyl chloroindonemalonate phenylhydrazone,



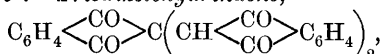
forms short, brown needles and melts at 144—145°.

Bromoindone resorcinol ether, $\text{CO} \begin{array}{c} \text{CBr} \\ \diagup \quad \diagdown \\ \text{C}_6\text{H}_4 \end{array} \text{C}\cdot\text{O}\cdot\text{C}_6\text{H}_4\cdot\text{OH}$, forms yellow needles and melts at 171°; the *acetyl* derivative separates from dilute acetic acid in yellow crystals and melts at 105°.

Ethylaminochloroindone, $\text{CO} \begin{array}{c} \text{CCl} \\ \diagup \quad \diagdown \\ \text{C}_6\text{H}_4 \end{array} \text{C}\cdot\text{NHEt}$, prepared by the action of ethylamine on the ethyl malonate derivative, forms short, red needles and decomposes at 188°. *Ethylaminobromoindone* forms red needles and decomposes at 151°. *Benzylaminochloroindone*, $\text{CO} \begin{array}{c} \text{CCl} \\ \diagup \quad \diagdown \\ \text{C}_6\text{H}_4 \end{array} \text{C}\cdot\text{NH}\cdot\text{CH}_2\text{Ph}$, forms red prisms and decomposes at 182°. Attempts to condense dibromoindone with 2 mols. of ethyl malonate gave only Gabriel and Michael's tribenzoylenebenzene (compare Liebermann and Bergami, Abstr., 1890, 514).

T. M. L.

Action of Iodine on Ethyl Sodiodiketohydrindenecarboxylate. By CARL LIEBERMANN and L. FLATOW (*Ber.*, 1900, 33, 2433—2439).—*Diiododiketohydrindene*, $\text{C}_6\text{H}_4 \begin{array}{c} \text{CO} \\ \diagup \quad \diagdown \\ \text{CO} \end{array} \text{Cl}_2$, prepared by the action of iodine on ethyl sodiodiketohydrindenecarboxylate, crystallises from acetic acid in small, yellow prisms and melts and decomposes at 199°. *Trisdiketohydrindene*,



produced under other conditions when less iodine is used, forms snow-white prisms and melts and decomposes at 266°; the *dipotassium* salt (of the enolic form) is green with a golden shimmer; the *barium* salt is red. *Anhydrotrisdiketohydrindene*, $\text{C}_{27}\text{H}_{12}\text{O}_5$, probably a pyrone

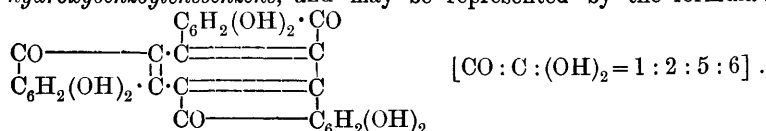
derivative, $\text{C}_6\text{H}_4 \begin{array}{c} \text{CO} \\ \diagup \quad \diagdown \\ \text{CO} \end{array} \text{C} \begin{array}{c} \text{CO}\cdot\text{C}_6\text{H}_4 \\ \diagup \quad \diagdown \\ \text{C}=\text{C} \\ \diagdown \quad \diagup \\ \text{C}=\text{C} \\ \diagup \quad \diagdown \\ \text{CO}\cdot\text{C}_6\text{H}_4 \end{array} \text{O}$, prepared by the action of acetic

acid and sodium acetate on trisdiketohydrindene, separates in golden-yellow scales, and does not melt at 320°.

T. M. L.

Trisdihydroxybenzoylenebenzene. By JOSEF LANDAU (*Ber.*, 1900, 33, 2440—2442).—The dark green substance (Abstr., 1898, i, 673) obtained from anhydrobisdimethoxydiketohydrindene is better prepared by heating the sodium derivative of ethyl dimethoxydiketohydrindenecarboxylate, $\text{C}_6\text{H}_2(\text{OMe})_2 \begin{array}{c} \text{CO} \\ \diagup \quad \diagdown \\ \text{CO} \end{array} \text{CNa}\cdot\text{CO}_2\text{Et}$, with fuming hydrochloric acid at 150°; it forms a very insoluble, black, granular powder, and has the formula $(\text{C}_9\text{H}_4\text{O}_3)_x$. Under similar conditions, anhydrobisketohydrindene is converted into tribenzoyl-

enebenzene, so that the dark green substance is probably *trisdi-hydroxybenzoylenebenzene*, and may be represented by the formula:



It forms a *hexabenzoyl* derivative when heated with benzoyl chloride at 150°. C. F. B.

2 : 2'-Dihydroxyflavone. By STANISLAUS VON KOSTANECKI and A. SEIFART (*Ber.*, 1900, 33, 2509—2512. Compare this vol., i, 448).—**2 : 2'-Diethoxyflavanone**, $\text{C}_{15}\text{H}_{10}\text{O}_2(\text{OEt})_2$, obtained by adding 50 per cent. sodium hydroxide solution to a hot alcoholic solution of 2-hydroxy-5-ethoxyacetophenone and *o*-ethoxybenzaldehyde, crystallises from alcohol in needles melting at 100—101°. It dissolves in concentrated sulphuric acid or alcoholic potassium hydroxide, yielding orange solutions; its alcoholic solution exhibits a blue fluorescence. The *monobromo*-derivative, $\text{C}_{15}\text{H}_9\text{BrO}_2(\text{OEt})_2$, crystallises in short needles, and melts at 101—102°.

2 : 2'-Diethoxyflavone, $\text{C}_{15}\text{H}_8\text{O}_2(\text{OEt})_2$, prepared by heating the preceding compound with alcoholic potassium hydroxide, crystallises in colourless needles melting at 106°; its solution in concentrated sulphuric acid is yellow with a green fluorescence.

The compound is hydrolysed by the action of sodium ethoxide, *o*-ethoxybenzoic acid and 2-hydroxy-5-ethoxyacetophenone resulting from the acidic fission, whilst the monoethyl ether of quinolcarboxylic acid is produced by the ketonic fission.

It was formerly stated that 3 : 2'-diethoxyflavone on hydrolysis yields salicylic acid, together with the monoethyl ether of resacetophenone (*Abstr.*, 1899, i, 524); in reality, the acidic fission gives rise to *o*-ethoxybenzoic acid. The product, which was taken to be salicylic acid, is the monoethyl ether of resorecylic acid, resulting from the ketonic fission.

2 : 2'-Dihydroxyflavone, produced by the action of hydrogen iodide on 2 : 2'-diethoxyflavone, is obtained in pale yellow needles melting at 304—305°; it dissolves in aqueous alkalis, yielding yellow solutions, and its solution in concentrated sulphuric acid is yellow with a green fluorescence. The *diacetyl* derivative forms colourless prisms and melts at 148—149°. G. T. M.

β -Methyl-2-hydroxychromone. By C. CRIVELLI and STANISLAUS VON KOSTANECKI (*Ber.*, 1900, 33, 2512—2513. Compare preceding abstract).—**2 : 5-Diethoxyacetylacetophenone**, $\text{C}_6\text{H}_3(\text{OEt})_2 \cdot \text{CO} \cdot \text{CH}_2 \cdot \text{COMe}$, obtained by mixing together 2 : 5-diethoxyacetophenone, ethyl acetate, and metallic sodium, acidifying with dilute acetic acid and extracting with ether, separates from dilute alcoholic solutions in colourless, flattened acicular crystals, and melts at 60°; its alcoholic solution is reddened by ferric chloride.

6-Hydroxy-2-methylchromone, $\text{OH} \cdot \text{C}_6\text{H}_4 \begin{array}{c} \text{O} \text{---} \text{CMe} \\ | \\ \text{CO} \cdot \text{CH} \end{array}$, produced from

the preceding compound by the prolonged action of hot hydriodic acid, crystallises in pale yellow prisms and melts at 247° ; it develops a yellow coloration when dissolved in alkalis; its solution in concentrated sulphuric acid is colourless with a greenish-blue fluorescence. The *acetyl* derivative crystallises in silky needles, and melts at 99° .

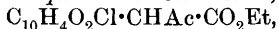
2:5-Diethoxybenzoylacetophenone, $C_6H_3(OEt)_2 \cdot CO \cdot CH_2 \cdot COPh$, prepared in a similar manner to the corresponding acetyl compound, crystallises in pale yellow, lustrous needles, and melts at $72-74^{\circ}$; its alcoholic solution develops a red coloration with ferric chloride. When heated with hydriodic acid, it is converted into 2-hydroxyflavone (compare Abstr., 1899, i, 370). G. T. M.

4'-Hydroxyflavone. By S. GROSSMANN and STANISLAUS VON KOSTANECKI (*Ber.*, 1900, 33, 2515—2517).—2:4'-Diethoxybenzoylacetophenone, prepared from ethyl 2-ethoxybenzoate and 4-ethoxyacetophenone by condensation with sodium (compare this vol., i, 239), crystallises from dilute alcohol in leaflets, and melts at $110-111^{\circ}$; on boiling for several hours with hydriodic acid of sp. gr. 1.9, it yields 4'-hydroxyflavone, $C_6H_4 \begin{matrix} \diagup O-C_6H_4 \cdot OH \\ | \\ CO \cdot CH \end{matrix}$, which crystallises from pyridine-alcohol in small, white tufts of needles, melts at 268° , and dissolves in concentrated sulphuric acid giving a solution with an intense blue fluorescence. 4'-Acetoxyflavone crystallises from dilute alcohol in white needles and melts at 137° . 4'-Ethoxyflavone, obtained by warming 2:4'-diethoxybenzoylacetophenone for only a short time with hydriodic acid of sp. gr. 1.7, crystallises from alcohol in white needles melting at $139-140^{\circ}$. W. A. D.

2:3-Dichloro- α -naphthaquinolyl Derivatives of β -Diketones. By FR. MICHEL (*Ber.*, 1900, 33, 2402—2411. Compare Liebermann, this vol., i, 310).—Plagemann's dichloronaphthaquinone (Abstr., 1882, 973) is produced in small quantities in the preparation of 2:3-dichloro- α -naphthaquinone from the calcium derivative of dinitronaphthol; with ethyl sodiomalonate, it gives a diethyl chloronaphthaquinonemalonate, $C_{10}H_4O_2Cl \cdot CH(CO_2Et)_2$, which forms a yellow, crystalline powder, melts at 86° , and gives a blue coloration with sodium ethoxide.

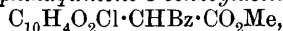
2-Chloro-3- α -cyanobenzyl- α -naphthaquinone, $C_{10}H_4O_2Cl \cdot CHPh \cdot CN$, prepared from 2:3-dichloro- α -naphthaquinone and the sodium derivative of benzyl cyanide, crystallises from alcohol in short, yellowish prisms, and melts at 184° .

Ethyl 2-chloro- α -naphthaquinone-3-acetoacetate,



prepared in a similar manner from ethyl sodioacetoacetate, separates from alcohol in yellow crystals and melts at $106-107^{\circ}$; ethyl 2-acetonyl- α -naphthaquinone-3-acetate (Liebermann, *loc. cit.*), is produced as a bye-product.

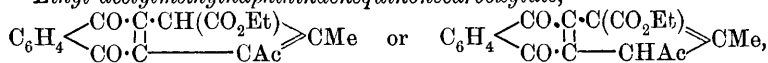
Methyl 2-chloro- α -naphthaquinone-3-benzoylacetate,



separates from methyl alcohol as a yellow, crystalline powder and melts at about $172-173^{\circ}$. 2-Chloro- α -naphthaquinone-3-acetylacetone,

$C_{10}H_4O_2Cl \cdot CHAc_2$, crystallises from dilute alcohol in yellow scales and melts at $131-132^\circ$.

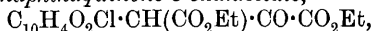
Ethyl acetylmethylnaphthindenequinonecarboxylate,



prepared by the action of sodioacetylacetone on ethyl chloro- α -naphthaquinoneacetoacetate, crystallises in minute, garnet-red needles and melts at 177° .

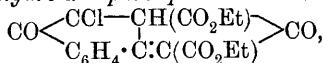
2-Chloro- α -naphthaquinone-3-benzoylacetone, $C_{10}H_4O_2Cl \cdot CHAcBz$, crystallises in large, yellow tablets from methyl alcohol and melts at 109° .

Diethyl 2-chloro- α -naphthaquinone-3-oxalacetate,



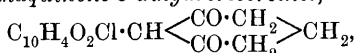
crystallises from alcohol in yellow, transparent prisms, melts at $117-118^\circ$, and loses carbon dioxide on further heating.

Diethyl 2-chloroanhydro- α -naphthaquinone-2-acetonedicarboxylate,



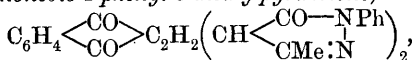
prepared by the action of diethyl sodioacetonedicarboxylate on dichloro- α -naphthaquinone, separates from alcohol as a dull yellow, crystalline powder and melts at $159-160^\circ$.

2-Chloro- α -naphthaquinone-3-dihydroresorcinol,



crystallises from alcohol in yellowish flakes melting at 258° .

α -Naphthaquinonebis-1-phenyl-3-methylpyrazolone,



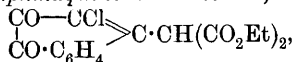
prepared by the action of sodiophenylmethylpyrazolone, crystallises from alcohol in clear, blood-red, glistening flakes.

Measurements are given of the crystals of ethyl chloro- α -naphthaquinoneacetoacetate, chloro- α -naphthaquinonebenzoylacetone, and diethyl chloro- α -naphthaquinoneoxalacetate. T. M. L.

Halogen-substituted β -Naphthaquinolyl Derivatives of β -Diketones. By H. HIRSCH (*Ber.*, 1900, 33, 2412-2418. Compare preceding abstract).

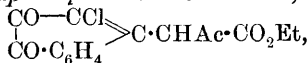
—*3-Chloro-2-bromo- β -naphthaquinone*, $C_6H_4 \begin{array}{c} \text{CO} \text{---} \text{CO} \\ \text{CBr} \text{---} \text{CCl} \end{array}$, crystallises from acetic acid in bronze-coloured, glistening plates and melts at 181.5° ; with aniline, it gives Zincke and Fröhlich's 3-chloro-2-hydroxy- α -naphthaquinoneanilide (*Abstr.*, 1887, 54).

Ethyl 3-chloro- β -naphthaquinone-4-malonate,



crystallises from alcohol in reddish-yellow prisms and melts at 97° .

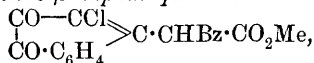
Ethyl 3-chloro- β -naphthaquinone-4-acetoacetate,



crystallises from acetic acid in red, glistening needles and melts at

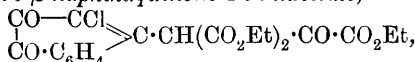
175°. 3-Chloro- β -naphthaquinone-4-acetylacetone, $\begin{array}{c} \text{CO}-\text{CCl} \\ | \\ \text{CO}\cdot\text{C}_6\text{H}_4 \end{array} \gg \text{C}\cdot\text{CHAc}_2$, crystallises from acetic acid in red needles and melts at 218°.

3-Chloro- β -naphthaquinone-4-benzoylacetone, $\begin{array}{c} \text{CO}-\text{CCl} \\ | \\ \text{CO}\cdot\text{C}_6\text{H}_4 \end{array} \gg \text{C}\cdot\text{CHAcBz}$, crystallises from acetic acid in dark-red, glistening tablets, and melts at 195°. Methyl 3-chloro- β -naphthaquinone-4-benzoylacetate,



is a red, crystalline powder and melts at 173°.

Diethyl 3-chloro- β -naphthaquinone-4-oxalacetate,



crystallises from alcohol in orange-red, glistening flakes, and melts at 127.5°.

3-Chloro- β -naphthaquinone-4-deoxybenzoin, $\begin{array}{c} \text{CO}-\text{CCl} \\ | \\ \text{CO}\cdot\text{C}_6\text{H}_4 \end{array} \gg \text{C}\cdot\text{CHPhBz}$,

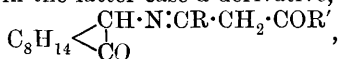
forms glistening, golden-yellow, felted needles and melts at 195.5°.

3-Bromo- β -naphthaquinone-4-acetylacetone, $\begin{array}{c} \text{CO}-\text{CBr} \\ | \\ \text{CO}\cdot\text{C}_6\text{H}_4 \end{array} \gg \text{C}\cdot\text{CHAc}_2$,

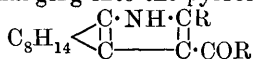
forms deep-red needles and melts at 212°.

T. M. L.

Synthetical Bases of the Series of Terpenes and Camphors : Pyrrole Derivatives of the Camphor Group. By PAUL DUDEN and W. TREFF (*Annalen*, 1900, 313, 25—58. Compare Abstr., 1899, i, 779).—Aminocamphor undergoes condensation with aldehydes and β -ketones, yielding in the latter case a derivative,



which, under the influence of sodium ethoxide, becomes converted into an isomeric dicyclic compound, $\text{C}_8\text{H}_{14} \begin{array}{c} \diagup \text{CH}\cdot\text{N}\cdot\text{CR} \\ \diagdown \text{C}(\text{OH})\cdot\text{CH}\cdot\text{COR}' \end{array}$; this readily loses water, changing into the pyrrole derivative,



The ring system, $\begin{array}{c} \text{C} \quad \text{C} \\ | \quad | \\ \text{C} \quad \text{C} \quad \text{N} \quad \text{C} \\ | \quad | \\ \text{C} \quad \text{C} \end{array}$, which forms the basis of these

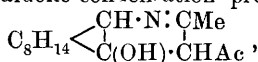
compounds, is entitled camphenepyrrole by the authors.

The pyrrole derivatives obtained in this way are distinguished as α -compounds, because they undergo isomeric transformation when treated with mineral acids, yielding the so-called β -compounds, which appear to be isopyrrole derivatives, $\text{C}_8\text{H}_{14} \begin{array}{c} \diagup \text{C}\cdot\text{N}\cdot\text{CR} \\ \diagdown \text{C} \quad \text{CH}\cdot\text{COR}' \end{array}$, containing tertiary nitrogen.

[In part with D. HEYNSIUS.]—Anhydroacetylacetoneaminocamphor, $\text{C}_8\text{H}_{14} \begin{array}{c} \diagup \text{CH}\cdot\text{N}\cdot\text{CMe}\cdot\text{CH}_2\cdot\text{CO}\cdot\text{CH}_3 \\ \diagdown \text{CO} \end{array}$, prepared by merely mixing ethereal

solutions of acetylacetone and freshly prepared aminocamphor, crystallises from a mixture of ether and petroleum in long, colourless needles, and melts at 88° ; mineral acids resolve it into the components.

3-Acetyl-2-methylcamphenepyrrole (α -derivative), $C_8H_{14} \begin{smallmatrix} & C \cdot NH \cdot CMe \\ & | & | \\ & C & - & CAc \end{smallmatrix}$, crystallises in colourless prisms melting at 231° , and in small quantities may be distilled at 325° ; it is obtained by recrystallising from glacial acetic acid the aldolic condensation product,

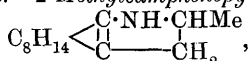


which results from anhydroacetylacetoneaminocamphor and sodium ethoxide, and crystallises from acetone, benzene, or alcohol in hexagonal leaflets melting at 150° . The acetyl derivative, $C_{17}H_{23}O_2N$, crystallises from methyl alcohol in long, slender needles melting at 88° , and the nitrosoamine, $C_{15}H_{20}N_2O_2$, separates from petroleum in yellowish prisms melting at 119° . Cinnamoylmethylcamphenepyrrole,

$C_8H_{14} \begin{smallmatrix} & C \cdot NH \cdot CMe \\ & | & | \\ & C & - & C \cdot CO \cdot CH \cdot CHPh \end{smallmatrix}$, produced by the action of benzaldehyde in presence of alkali, crystallises from a mixture of ether and petroleum in orange-yellow leaflets which melt to a reddish-brown liquid at 180° .

3-Acetyl-2-methylcamphenepyrrole (β -derivative), $C_8H_{14} \begin{smallmatrix} & C \cdot N \cdot CMe \\ & | & | \\ & C & - & CHAc \end{smallmatrix}$, formed when the α -modification is heated with dilute mineral acids, crystallises from light petroleum in slender needles melting at 134 — 135° ; it resists the action of reducing agents which attack the isomeride, and is also indifferent towards acetic anhydride.

3-Acetyl-2-methylcamphenepyrroline, $C_8H_{14} \begin{smallmatrix} & C \cdot NH \cdot CHMe \\ & | & | \\ & C & - & CHAc \end{smallmatrix}$, obtained by reducing α -acetylmethylcamphenepyrrole with zinc dust and glacial acetic acid, is a colourless, alkaline, viscous oil which boils at 226 — 228° under 120 mm. pressure, has a sp. gr. 1.0164 at $9^{\circ}/4^{\circ}$, and refractive index 1.5005 at 9° ; it has a camphor-like odour, and distils slowly in steam. The picrate crystallises in a network of small needles and melts at 133 — 134° ; precipitates are formed with mercuric chloride, copper sulphate, and silver nitrate, but they are not characteristic. Oxidation by Tafel's method (Abstr., 1894, i, 301) regenerates acetylmethylcamphenepyrrole. 2-Methylcamphenepyrroline,

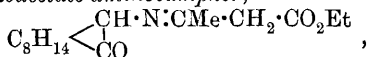


a bye-product in the formation of methylacetylcamphenepyrroline, boils at 210 — 212° under 120 mm. pressure; the picrate melts at 213° .

When 3-acetyl-2-methylcamphenepyrroline is reduced with sodium amalgam in ice-cold dilute hydrochloric acid, 2-methyl-3-hydroxyethylcamphenepyrrolidine, $C_8H_{14} \begin{smallmatrix} & CH \cdot NH \cdot CHMe \\ & | & | \\ & CH & - & CH \cdot CHMe \cdot OH \end{smallmatrix}$, is produced in two modifications, of which the one more soluble in ether (A) crystallises from petroleum in highly refractive prisms melting at 130 — 131° ,

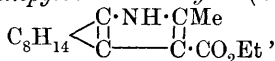
and forms the *picrate* and *platinichloride* melting and decomposing at 220—221° and 183—185° respectively; the isomeride (B), which is sparingly soluble in ether or petroleum, crystallises from alcohol in needles which melt at 222°, the *picrate* and *platinichloride* melting at 187° and 129—130° respectively, the latter decomposing.

Anhydroethylacetoacetate-aminocamphor,



obtained from ethyl acetoacetate and freshly prepared aminocamphor, crystallises from petroleum in long, colourless needles melting at 58°.

Ethyl 2-methylcamphenepyrrole-3-carboxylate (α -derivative),

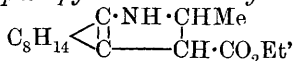


crystallises from ether or petroleum in colourless, rectangular leaflets, melts at 198°, and boils at 330°, slightly decomposing; the *acetyl* derivative, $\text{C}_{18}\text{H}_{25}\text{O}_3\text{N}$, also forms colourless, rectangular leaflets, which melt at 63—64°, and the *nitrosoamine*, $\text{C}_{16}\text{H}_{22}\text{O}_3\text{N}_2$, separates from petroleum in small needles melting at 126—127°. The ester is somewhat indifferent towards hydrolytic agents, but alcoholic potash at 125° eliminates carbon dioxide, forming the *base*, $\text{C}_{13}\text{H}_{21}\text{ON}$, which melts at 136°, and yields the *picrate* melting at 141—142°. The

β -derivative, $\text{C}_8\text{H}_{14} \begin{array}{c} \text{C} \cdot \text{N} \cdot \text{CMe} \\ \diagup \quad \diagdown \\ \text{C} \quad \text{CH} \cdot \text{CO}_2\text{Et} \end{array}$, crystallises from dilute alcohol in aggregates, and melts at 124—125°; it is hydrolysed by alcoholic potash, forming β -methylcamphenepyrrolecarboxylic acid, $\text{C}_8\text{H}_{14} \begin{array}{c} \text{C} \cdot \text{N} \cdot \text{CMe} \\ \diagup \quad \diagdown \\ \text{C} \quad \text{CH} \cdot \text{CO}_2\text{H} \end{array}$, which darkens at 195°, melts, evolving gas, at 210°, and forms sodium, calcium, lead, copper, and silver salts which are not characteristic.

2-Methylcamphenepyrrole, $\text{C}_8\text{H}_{14} \begin{array}{c} \text{C} \cdot \text{NH} \cdot \text{CMe} \\ \diagup \quad \diagdown \\ \text{C} \quad \text{CH} \end{array}$, prepared by heating dried sodium β -methylcamphenepyrrolecarboxylate with lime, is a yellowish, viscous oil which crystallises in melting ice and boils at 220—224° under 210 mm. pressure.

Ethyl 2-methylcamphenepyrroline-3-carboxylate,



obtained by reducing ethyl methylcamphenepyrrolecarboxylate with zinc dust and acetic acid, boils at 245—246° under 207 mm. pressure and at 293—295° under atmospheric pressure; it is a strongly alkaline, viscous oil with an agreeable odour of peppermint.

Anhydrobenzoylacetoneaminocamphor, $\text{C}_8\text{H}_{14} \begin{array}{c} \text{CH} \cdot \text{N} \cdot \text{CMe} \cdot \text{CH}_2 \\ \diagup \quad \diagdown \quad \diagdown \\ \text{CO} \quad \quad \text{COPh} \end{array}$, crystallises from alcohol in long, colourless prisms, and melts at 111°; mineral acids resolve it into the components.

3-Benzoyl-2-methylcamphenepyrrole, $\text{C}_8\text{H}_{14} \begin{array}{c} \text{C} \cdot \text{NH} \cdot \text{CMe} \\ \diagup \quad \diagdown \\ \text{C} \quad \text{C} \cdot \text{COPh} \end{array}$, crystallises from benzene in pale yellow prisms and melts at 256°; the *acetyl* derivative crystallises from methyl alcohol in colourless prisms melting

at 104—105°, and the *phenylhydrazone* separates from benzene in leaflets melting at 132°. M. O. F.

Synthetical Bases of the Series of Terpenes and Camphors: Camphenamine and β -isoCamphor. By PAUL DUDEN and ALFRED E. MACINTYRE (*Annalen*, 1900, 313 59—79. Compare this vol., i, 302).—The authors have studied the action of nitrous acid on camphenamine, $C_8H_{14} \begin{smallmatrix} \text{C} \cdot \text{NH}_2 \\ | \\ \text{CH} \end{smallmatrix}$, expecting to obtain the enolic form of a ketone, $C_{10}H_{16}O$, which would differ from natural camphor in the mutual displacement of the carbonyl and methylene groups; the product, however, although having the anticipated empirical formula, is an unsaturated alcohol, and is quite indifferent towards hydroxylamine, semicarbazide, or sodium in alcohol. The name β -isocamphor is chosen by the authors for this compound.

[In part with J. ROBERTSON.]— β -Aminoborneol, $C_8H_{14} \begin{smallmatrix} \text{CH} \cdot \text{NH}_2 \\ | \\ \text{CH} \cdot \text{OH} \end{smallmatrix}$, stereoisomeric with α -aminoborneol (*Abstr.*, 1898, i, 677), and produced along with that substance when aminocamphor is reduced in boiling alcohol with excess of sodium, melts at 166° and boils at 262—263° under 751 mm. pressure; the specific rotatory power is $[\alpha]_D -42.46^\circ$ in methyl alcohol, that of the α -modification being $[\alpha]_D -8.73^\circ$ in the same medium. The *aurichloride* forms slender needles melting at 227°; the *platinichloride* crystallises in leaflets melting at 293°; the *carbamide* melts at 211°, and the *acetyl* derivative at 130°. Attempts to withdraw the elements of water from aminoborneol by means of concentrated sulphuric acid, phosphoric oxide, phosphoric acid, concentrated hydrochloric acid, zinc chloride, and phosphorus pentasulphide have been unsuccessful. In order to arrive at camphenamine, therefore, it was necessary to convert aminoborneol first into chlorocamphanamine, and then eliminate hydrogen chloride from that compound (this vol., i, 302).

Chlorocamphanamine, $C_8H_{14} \begin{smallmatrix} \text{CH} \cdot \text{NH}_2 \\ | \\ \text{CHCl} \end{smallmatrix}$, is an oil which suddenly solidifies to the hydrochloride of camphenamine when an attempt is made to distil it; its *hydrochloride* crystallises in needles, and melts at 255°. The *platinichloride* decomposes above 260°, and the *picrate* melts at 190—191°.

Camphenamine, $C_8H_{14} \begin{smallmatrix} \text{C} \cdot \text{NH}_2 \\ | \\ \text{CH} \end{smallmatrix}$, is a colourless, mobile oil with a sweet, characteristic odour; it boils at 160—161° and at 205—207° under pressures of 200 mm. and 748 mm. respectively. It has a sp. gr. 0.9399 at 20°, and the refractive index 1.4935 at 20°; the specific rotatory power is $[\alpha]_D -4.15^\circ$ in methyl alcohol. The *hydrochloride*, *sulphate*, and *nitrate* decompose at 250°, 272°, and 198—199° respectively; the *platinichloride*, *aurichloride*, and *picrate* melt and decompose at 267—268°, 157—158°, and 214—215° respectively, whilst the *zinc double salt*, $ZnSO_4(C_{10}H_{17}N)_2 \cdot H_2SO_4 \cdot 6H_2O$, crystallises from water in lustrous leaflets and decomposes above 280°. The

acetyl derivative melts at 100° , and the *carbamide* separates from methyl alcohol in long prisms melting at 190° .

β -iso*Camphor*, $\text{OH} \cdot \text{C}_8\text{H}_{13} \begin{smallmatrix} \text{CH} \\ | \\ \text{CH} \end{smallmatrix}$, prepared by the action of nitrous acid on camphenamine, sublimes in long needles having the odour and appearance of camphor, and melts at 102° ; the specific rotatory power is $[\alpha]_{\text{D}} + 17.65^{\circ}$ in methyl alcohol. The substance decolorises bromine in chloroform, combines with hydrogen bromide, and reduces alkaline permanganate. The *phenylurethane*, $\text{C}_{17}\text{H}_{21}\text{O}_2\text{N}$, crystallises from petroleum or dilute methyl alcohol in long needles melting at 112° .

M. O. F.

Camphordioximes. By FRANCESCO ANGELICO (*Atti Real. Accad. Lincei*, 1900, [v], 9, ii, 47—51).—By boiling bromopernitrosocamphor with excess of hydroxylamine hydrochloride and sodium hydroxide in dilute alcoholic solution, and then passing a current of carbon dioxide through the liquid, the camphor- β -dioxime of Manasse is obtained; but when the hydroxylamine acts in the presence of sodium acetate, the products are the α -dioxime and a new isomeride to which the name *camphor- δ -dioxime* is given. The latter is slightly soluble in alcohol, melts at about 245° , and gives a *dibenzoyl* derivative melting at 188° . The α - and δ -dioximes are also obtained when bromocamphor is boiled in aqueous alcoholic solution with hydroxylamine hydrochloride and sodium acetate. Four isomeric camphordioximes have now been prepared, this being the first instance in which all the isomeric dioximes of an asymmetrical diketone are known.

T. H. P.

Fenchone. By HANS CZERNY (*Ber.*, 1900, 33, 2287—2294).—*Bromofenchone*, $\text{C}_{10}\text{H}_{15}\text{OBr}$, obtained by heating fenchone with bromine for 20 hours at 100° in a sealed tube, is a colourless oil which boils at 131 — 134° under 18 mm. pressure, has a faint camphor-like odour, a sp. gr. 1.348 at 12° , a refractive index 1.51013, and a rotation $+11.6^{\circ}$ in a 100 mm. tube. It is not readily volatile with steam, and yields neither an oxime nor a semicarbazone. When a solution in acetone is heated under pressure at 130 — 140° with freshly precipitated silver oxide, the substance is not attacked. If the compound is heated with zinc dust and acetic acid, fenchone is regenerated.

When bromofenchone is heated with excess of strong alcoholic potassium hydroxide, fencholenic acid is produced, identical with that obtained by Wallach (*Abstr.*, 1891, 219; 1892, 1237); it has a refractive index 1.4734 and sp. gr. 1.008 at 22° ; when cooled with liquid air, it crystallises. The acid dissolves easily in concentrated sulphuric acid, and if the solution is poured on ice, an isomeric compound, $\text{C}_{10}\text{H}_{16}\text{O}_2$, separates, which melts at 77° and crystallises from light petroleum in leaflets; it neither dissolves in solutions of sodium carbonate or hydroxide nor decolorises solutions of potassium permanganate.

Tribromofenchane, $\text{C}_{10}\text{H}_{15}\text{Br}_3$, formed by the gradual addition of bromine to a solution of fenchone in phosphorus trichloride, is a yellow oil which boils at 181 — 186° under 18 mm. pressure, and rapidly darkens in the air; it does not crystallise, but when cooled with

liquid air, solidifies to a vitreous mass. When tribromofenchane is boiled with zinc dust and acetic acid, it yields a crystalline *substance*, $C_{10}H_{15}Br$, which melts at $115-116^\circ$, has a camphor-like odour, sublimes very readily, decolorises solution of potassium permanganate, and in its general properties resembles the chlorofenchene of Gardner and Cockburn (Trans., 1897, 71, 1157; 1898, 73, 704).

E. G.

Carvotanacetone, Tanacetone, and Terpenone, $C_{10}H_{16}O$, (from Tetrahydrocarvone). By FRIEDRICH W. SEMMLER (*Ber.*, 1900, 33, 2454—2459).—Carvotanacetone is different from dihydrocarvone (compare Abstr., 1895, i, 675) and carvenone (Abstr., 1899, i, 225); from its direct reduction by sodium (to tetrahydrocarvone) the presence of a $C:C:CO$ group may be inferred. When oxidised with dilute aqueous permanganate at 0° , it is now found to take up 60 per mol., and yield pyruvic and isopropylsuccinic acids; hence its formula must be $CH_2 \begin{smallmatrix} \text{CHPr}^\beta \cdot CH_2 \\ \text{CH} = CMe \end{smallmatrix} > CO$, and it is an "ortho" derivative (this vol., i, 453). In harmony with this constitution is the fact that it unites with hydrogen sulphide in ammoniacal solution; the product melts at about 95° , and is probably identical with a substance obtained by Wallach and Schrader (Abstr., 1894, i, 537) from the high boiling fraction of thuja oil. In the conversion of tanacetone into carvotanacetone (Abstr., 1894, i, 339), it is thus the meta-bond of the former (this vol., i, 241) that disappears.

The existence of this meta-bond is maintained, as opposed to the para-bond assumed by Fromm (this vol., i, 402).

Von Baeyer's terpenone, $C_{10}H_{16}O$, yields an acid, $C_9H_{16}O_4$, when oxidised, and this yields isopropylsuccinic acid when further oxidised. Probably terpenone has the formula $CH_2 \begin{smallmatrix} \text{CHPr}^\beta - CH_2 \\ \text{CH}_2 \cdot C(:CH_2) \end{smallmatrix} > CO$, and is the pseudo-form corresponding with carvotanacetone. C. F. B.

Oil of Turpentine. By CHAS. T. TYRER and ALFRED WERTHEIMER (*Pharm. J.*, 1900, [iv], 11, 101—104).—Exhaustive fractionation of large quantities of American turpentine failed to show any optically inactive portion. About 0.5 per cent. boiling between 160.2° and 160.4° had a rotation of -0.04° (measured in a 188.6 mm. tube); of 21 fractions the last eleven were levorotatory, the limit being -10.3° .

R. L. J.

Viscosity of Essential Oils. By EDWIN DOWZARD (*Pharm. J.*, 1900, [iv], 11, 100).—The viscosity numbers of a series of oils as determined in a Reischauer viscometer, are: Lime, 177; bergamot, 219.8; orange, 112.5; citronella, 536; rosemary, 320; winter green, 261; sassafras, 238; lemon, 139.6. For citrene, the value is 106.8 and for a mixture of citrene and citral (7.5 per cent.) 114.9.

R. L. J.

Ethereal Oil of Fir Wood (*Pinus abies*, L.). By PETER KLASON (*Ber.*, 1900, 33, 2343—2344).—The wood of the fir-tree, employed in the preparation of sulphite cellulose, yields an oil which has been

usually regarded as oil of turpentine. An examination of this substance, however, has shown it to be cymene. M. O. F.

Crystallised Constituent of the Essential Oil of *Kaempferia Galanga*, L. By PIETER VAN ROMBURGH (*Proc. K. Akad. Wetensch. Amsterdam*, 1900, 3, 38—41).—The rhizomes of *Kaempferia Galanga*, L., when distilled with steam, yield two volatile products, a light oil containing terpenoid substances and a heavy oil depositing crystals.

The crystalline product is ethyl *p*-methoxycinnamate, its properties corresponding exactly with those of the compound obtained from anisaldehyde and ethyl acetate (Vorländer, *Abstr.*, 1897, i, 275). The ester is readily hydrolysed by potassium hydroxide, and the corresponding acid is identical with the *p*-methoxycinnamic acid obtained by Knoevenagel (*Abstr.*, 1899, i, 145) from anisaldehyde and malonic acid; it melts at 169° to an opalescent liquid which becomes translucent at 185°. On reducing the substance in alcoholic solution with sodium amalgam, *p*-methoxypropionic acid is produced. G. T. M.

German Rose Oil. By HEINRICH WALBAUM and KARL STEPHAN (*Ber.*, 1900, 33, 2302—2308).—In addition to geraniol, always present in German rose oil (Bertram and Gildemeister, *Abstr.*, 1894, i, 253), the authors have found small quantities of normal *nonaldehyde* (which boils at 80—82° under 30 mm. pressure, has a density 0·8277 at 15°, and a molecular refraction n_D at 16° 1·42452) and of linalool, citral, phenyl-ethyl alcohol and citronellol. R. H. P.

Constituents of East Indian Sandalwood Oil. By HUGO VON SODEN (*Arch. Pharm.*, 1900, 238, 353—366. Compare *Abstr.*, 1899, i, 924, and Guerbet, this vol., i, 242, 401).—Santalol, known commercially as gonorol, is prepared from sandalwood oil by heating it with a little alcoholic potash, precipitating and washing the oil with water, and fractionating it under diminished pressure; the higher boiling part is santalol, and amounts to about 80 per cent. of the oil; the rest consists largely of sesquiterpenes. By repeated fractionation, conversion of appropriate fractions into santalylphthalic acids and regeneration of the santalol from these, an approximate separation into two substances was effected. α -Santalol is probably a sesquiterpene alcohol, $C_{15}H_{23}\cdot OH$, and forms the chief constituent of "santalol" and East Indian sandalwood oil. It is a thick, colourless liquid with a faint odour of sandalwood, has a sp. gr. 0·977 at 15°, is feebly dextrorotatory, and boils at 301—302°, and 155° under pressures of 1 atm. and 8 mm. respectively; α -santalyl acetate has a sp. gr. 0·988 at 15°, is dextrorotatory, and boils at 311—312°. β -Santalol, perhaps also $C_{15}H_{24}O$, has a rotation exceeding -45° . C. F. B.

East Indian Sandalwood Oil. By FRIEDRICH MÜLLER (*Arch. Pharm.*, 1900, 238, 366—383).—The first fractions obtained in distilling East Indian sandalwood oil (from the wood of *Santalum album*, L.) were freed from acid by shaking with dilute aqueous sodium hydroxide, and then fractionated repeatedly under 15 mm. pressure; the fraction boiling above 135°, which consisted largely of sesquiterpenes, was neglected. Even then one fraction, boiling mostly at 126°, con-

sisted of a sesquiterpene; in addition, two other substances were isolated, and these are described below.

Santene, C_9H_{14} , a lower homologue of the terpenes, boils at $35-37^\circ$ and $139-140^\circ$ under 15 mm. and 1 atmo. pressure respectively, and has a sp. gr. 0.8710 at 15° . When treated in cooled acetic acid solution with ethyl nitrite and strong hydrochloric acid, it forms a blue, soluble *nitrosochloride* which melts and decomposes at 108° ; this changes gradually into a colourless modification (polymeride?), which at 90° is reconverted into the blue substance. No well characterised nitrolamine could be obtained, and although a crystalline, blue nitrosite was prepared, it seemed to be a mixture of two substances. By treatment with hydrogen chloride in ethereal solution an unstable *mono-hydrochloride*, melting at about 80° , was prepared. With bromine in chloroform solution, santene yields a *tribromide*, $C_9H_{13}Br_3$, which melts at $62-63^\circ$.

Another fraction consisted of two ketones which were separated by means of their semicarbazones. That one of which the *semicarbazone* is more soluble in alcohol and has the lower melting point, 175° , is present in the larger amount; it is named *santalone*, $C_{11}H_{16}O$. It boils at $88-89^\circ$ and $214-215^\circ$ under 15 mm. and 1 atmo. pressure respectively, has a sp. gr. 0.9906 at 15° , and a rotation -62° in a 100 mm. tube; it forms an *oxime* which melts at $74.5-75.5^\circ$, and also a hydrobromide. The other ketone has not yet been investigated; its *semicarbazone* melts at 224° .

The acid obtained by shaking the first fractions of the sandalwood oil with aqueous sodium hydroxide, or the oil itself with aqueous sodium hydrogen carbonate, consists chiefly of tere-santallic acid, $C_9H_{13}\cdot CO_2H$ (compare Guerbet, this vol., i, 242); its *silver* salt was analysed. In cooled methyl alcoholic solution, it combines with hydrogen chloride; the *hydrochloride* formed, $C_9H_{14}Cl\cdot CO_2H$, melts and decomposes at 193° . When shaken with cold dilute caustic soda, this hydrochloride forms a *lactone*, $C_9H_{14}\begin{smallmatrix} \diagup CO \\ | \\ O \end{smallmatrix}$, which melts at 103° ; when boiled with the

alkali, it forms, not an acid, $OH\cdot C_9H_{14}\cdot CO_2H$, but apparently an *oxy-hydroditeresantallic acid*, $O(C_9H_{14}\cdot CO_2H)_2$, which melts at $143-144^\circ$; the *silver* salt of this acid was prepared and analysed. When a mixture of calcium teresantalate and acetate was distilled, a *hydrocarbon*, C_7H_{10} , boiling at $105-110^\circ$, and with a sp. gr. 0.818 at 15° , was obtained as the chief product. When teresantallic acid is boiled with dilute sulphuric acid, the chief product is a hydrocarbon, C_9H_{14} , *a-santene*, possibly identical with the santene previously described; it boils at $140-142^\circ$, has a sp. gr. 0.870 at 15° , and is inactive; its *tribromide* and *hydrochloride* melt at $53-54^\circ$ and about 65° respectively. The alkaline liquid obtained by heating sandalwood oil with alcoholic potash (von Soden, preceding abstract) also contains teresantallic acid. This acid occurs in the oil to the extent of about 0.5 per cent., forming about half of the total acid present.

C. F. B.

The Balsam of *Abies canadensis* (Canada Balsam). By ALEXANDER TSCHIRCH and ED. BRÜNING (*Arch. Pharm.*, 1900, 238, 487-504).—From an ethereal solution of the balsam, dilute aqueous

ammonium carbonate extracts amorphous *canadic acid*, $C_{19}H_{34}O_2$; this melts at $135-136^\circ$ and neutralises 1KOH as well in the cold as on boiling. Dilute aqueous sodium carbonate then extracts a mixture of acids; of these, amorphous *α -canadinolic acid*, $C_{19}H_{30}O_2$, melting at $89-95^\circ$, is precipitated by alcoholic lead acetate, whilst an isomeric *β -acid*, also amorphous and melting at $90-95^\circ$, remains in solution together with *canadolic acid*, $C_{19}H_{28}O_2$, which is crystalline and melts at $143-145^\circ$; both canadinolic acids neutralise 1KOH as well in the cold as on heating; canadolic acid neutralises 1KOH in the cold, and nearly 2 on heating.

The residual ethereal solution is washed with aqueous potassium hydroxide, the ether distilled off, and the residue distilled with steam; an *ethereal oil* distils over, boiling at $160-167^\circ$, whilst *canadorenen*, $C_{21}H_{40}O$, remains behind; this is amorphous, melts at 170° , and is indifferent to alkalis. Some canadorenen also separates in the solid state during the extraction of the original ethereal solution with sodium carbonate.

The balsam also contains an alkaloid soluble in water. In the dry distillation of the balsam, formic, acetic, and succinic acids are formed.

In 100 parts of the drug there are contained: canadic acid, 13; canadolic acid, 0.3; α - and β -canadinolic acids (α in much larger amount), 48-50; ethereal oil, 23-24; canadorenen, 11-12; succinic acid, alkaloid, and impurities, 1-2.

The acids seem to contain no methoxyl groups. In contradistinction to the resen, the acids give the cholesterol reactions, including Tschugaeff's reaction (*Zeit. angew. Chem.*, 1900, No. 25), which is well fitted to distinguish between acids and resens. C. F. B.

The Balsam of Abies Pectinata (Strasburg Turpentine). By ALEXANDER TSCHIRCH and G. WEIGEL (*Arch. Pharm.*, 1900, 238, 411-427).—The investigation was conducted in a similar manner to that of larch turpentine (next abstract), and gave similar results. From the ethereal solution of the turpentine 1 per cent. ammonium carbonate solution extracted abienic acid; with 1 per cent. sodium carbonate solution, acids were extracted from the solution of which in alcohol abietolic acid crystallised whilst α - and β -abietinolic acids remained dissolved; these could be separated by adding alcoholic lead acetate, which precipitated the α -, but not the β -acid. The ethereal solution remaining, after removal of the ether, was distilled with steam, when an ethereal oil came over, whilst abietoresen remained behind.

Abienic acid, $C_{13}H_{20}O_2$, is an amorphous substance, and melts at $114-115^\circ$; in the cold, it unites but slowly with enough $N/2$ potassium hydroxide to form a monopotassium salt. *Abietolic acid*, $C_{20}H_{28}O_2$, is crystalline but rather unstable; it melts at $145-153^\circ$; when titrated with $N/2$ potassium hydroxide, it seems to form in the cold a monopotassium salt, and when heated a dipotassium salt. α - and β -*Abietinolic acids* melt respectively at $95-96^\circ$ and $93-94^\circ$; both are amorphous, but have approximately the composition represented by $C_{16}H_{24}O_2$, and both seem to form monopotassium salts when titrated with $N/2$ potassium hydroxide, but gradually take up still more potassium.

Abietoresen, $C_{19}H_{13}O$, is amorphous, melts at $168-169^{\circ}$, and is different in its chemical character. The *ethereal oil* boils for the most part at $162-163^{\circ}$, but higher boiling fractions are also present.

In 100 parts of the drug are contained : abienic acid, 8—10 ; abietolic acid, 1.5—2 ; α - and β -abietinolic acids, 46—50 ; ethereal oil, readily volatile, 24—25, slightly volatile, 4—6 ; abietoresen, 12—16 ; alkaloid, colouring-matter, water, and impurities, 1—2 ; succinic acid, 0.05—0.08.

C. F. B.

The Balsam of Larix Decidua (Larch Turpentine). By ALEXANDER TSCHIRCH and G. WEIGEL (*Arch. Pharm.*, 1900, 238, 387—410).—This turpentine is collected chiefly in the Tyrol ; the method adopted and the regulations in force are described at length. It was dissolved in ether, and the resin acids were extracted by repeated shaking with 1 per cent. aqueous sodium carbonate, finally with sodium hydroxide. The ether was then distilled off, and the residue distilled with steam, when an ethereal oil came over and an amorphous *resen* remained behind. Traces of succinic acid were obtained when the turpentine was submitted to dry distillation, and an alkaloidal substance was also present ; esters were absent.

The resin acids were precipitated by acidifying the aqueous sodium carbonate solution, and dissolved in cold alcohol. When the solution was left for a time, *laricinolic acid*, $C_{20}H_{30}O_2$, melting at $147-148^{\circ}$, crystallised out. This reacts ordinarily as a monobasic acid ; its *potassium, silver, calcium, and lead* salts were analysed. In the presence of excess of potassium hydroxide, it gradually takes up more potassium ; when neutralised (to litmus paper) in alcoholic solution with alcoholic potash, it formed a salt, $C_{20}H_{29}O_2K, 3C_{20}H_{30}O_2$. It does not contain methoxyl, and it will not form either an ester or an acetyl derivative. The acids remaining in the alcoholic mother liquor were precipitated in part by alcoholic lead acetate, in part not. These two parts, α - and β -*larinolic acids* respectively, both have a composition corresponding with $C_{18}H_{26}O_2$, and are similar in their properties ; they are perhaps identical. On titration with potassium hydroxide, they react as monobasic acids, but in the presence of excess of the alkali they take up more potassium. All these acids resemble the *cholesterols* in their colour reactions.

The *resen* could not be obtained in a form that invited investigation.

The *ethereal oil* resembled oil of turpentine in general ; it can be separated into two parts, boiling at about 157° and 190° respectively.

The drug contains the following amounts of the different constituents in 100 parts. Laricinolic acid, 4—5 ; α - and β -larinolic acid, 55—60 ; ethereal oil, readily volatile, 15—16, slightly volatile, 5—6 ; *resen*, 14—15 ; alkaloid, colouring-matter, and impurities, 2—4 ; succinic acid, 0.1—0.12.

C. F. B.

Plumieride and its Identity with Agoniadin. By ANTOINE P. N. FRANCHIMONT (*Proc. K. Akad. Wetensch. Amsterdam*, 1900, 3, 35—38).—The author confirms his previous conclusions with regard to the identity of plumieride with agoniadin (*Abstr.*, 1899, i, 933), and proposes to retain the former term as the name of the substance.

G. T. M.

Luteolin Methyl Ether as a Product of the Hydrolysis of a Glucoside from Parsley. By EDUARD VONGERICHTEN (*Ber.*, 1900, 33, 2334—2342).—In addition to apiin, which, when hydrolysed, yields apigenin (A. G. Perkin, *Trans.*, 1897, 71, 805), and dextrose, parsley contains a second glucoside, which is probably oxyapiin methyl ether and, when hydrolysed, yields luteolin methyl ether and dextrose. *Luteolin methyl ether*, $C_{16}H_{12}O_6$, crystallises from alcohol in small needles melting at 250° , forms a *triacetyl* derivative, which crystallises in clusters of needles melting at 195° , a *tribenzoyl* derivative, which crystallises in slender needles melting at 235° , and can be easily converted into luteolin trimethyl ether (A. G. Perkin, *Trans.*, 1896, 69, 211, 799).
R. H. P.

The Fruits of Rhamnus Cathartica. By ALEXANDER TSCHIRCH and R. POLACCO (*Arch. Pharm.*, 1900, 238, 459—477).—When the berries of *Rhamnus cathartica* are percolated with water, the percolate extracted with ether, and the substances so extracted crystallised from alcohol, *rhamnocitrin*, $C_{13}H_{10}O_5$, separates; this forms yellow crystals, fluoresces when dissolved in sulphuric acid, melts at $221-222^{\circ}$, and forms a colourless *triacetyl* derivative melting at $199-200^{\circ}$; it is probably a trihydroxydihydrofluorone or dihydroxanthone. When the alcoholic extract is evaporated and the residue treated with toluene, *rhamnolutin*, $C_{15}H_{10}O_6$, remains undissolved (mixed with a little of a yellow substance, $C_{14}H_{10}O_6$); it forms yellow crystals, fluoresces in sulphuric acid, melts above 260° , and forms a colourless *tetracetyl* derivative melting at $182-183^{\circ}$; it is possibly a tetrahydroxyflavone. In the toluene is dissolved a little *rhamnochrysin*, $C_{13}H_{12}O_7$, which forms orange-yellow crystals and melts at $225-226^{\circ}$. In older berries, less rhamnocitrin and more rhamnochrysin is found. When the aqueous percolate, after extraction with ether, is hydrolysed with dilute sulphuric acid, ether then extracts β -*rhamnocitrin*, $C_{13}H_{10}O_5$, along with rhamnocitrin itself, which settles less rapidly from alcohol; the new substance melts above 260° , and forms a *diacetyl* derivative melting at $190-191^{\circ}$.

When the berries, already exhausted with water, are percolated with 1 per cent. ammonia, the percolate acidified with hydrochloric acid, and the precipitate extracted with alcohol, a little emodin dissolves, and a nigrin, insoluble also in ether and acetone, remains. *Rhamno-emodin*, $C_{15}H_{10}O_5$, is orange-red, melts at $254-255^{\circ}$, and resembles frangula-emodin greatly. *Rhamnonigrin* (C 56.3, H 5.3 per cent.) yields chrysammic acid when boiled with nitric acid; probably it was formed to a large extent from emodin compounds during the working up of the drug.

The purgative action is ascribed to the emodin. In addition to the substances enumerated, there are present an amorphous sugar, pectin, gummy substances, alkaloids, chlorophyll, fats, and a colouring-matter.

C. F. B.

Senna. By ALEXANDER TSCHIRCH and E. HIEPE (*Arch. Pharm.*, 1900, 238, 427—449).—From an aqueous percolate of senna leaves an unstable, yellowish, crystalline substance of the composition $C_{14}H_{10}O_5$ was deposited. The percolate yielded an impure cathartic acid

when concentrated and mixed with alcohol; when hydrolysed with dilute sulphuric acid, it yielded yellow, unstable, crystalline *sennarhamnetin*, which remains unmelted at 260° . A sample of cathartic acid obtained from Merck yielded senna-emodin and senna-chrysophanic acid when hydrolysed with boiling alcoholic potash.

A crude *anthraglucosennin* was obtained by percolating senna leaves with very dilute ammonia, and precipitating the extract with hydrochloric acid. It was extracted first with ether; when the substances extracted thereby are treated with toluene, there is left yellow, crystalline *glucosennin*, $C_{22}H_{18}O_8$, which remains unmelted at 260° , and reduces Fehling's solution only after hydrolysis with dilute sulphuric acid; from the toluene solution, light petroleum precipitates orange-red, crystalline *senna-emodin*, $C_{15}H_{10}O_5$ (which melts at $223-224^{\circ}$ and forms a yellow, crystalline *triacetyl* derivative melting at 170°), whilst yellow, crystalline *sennachrysophanic acid*, $C_{15}H_{10}O_4$, melting at 172° , remains dissolved. (Senna-emodin appears to be identical with aloe-emodin, but different from rheum-emodin and frangula-emodin, which again are identical. Glucosennin is a derivative of hydroxymethylantranthraquinone, and is probably an emodin-glucoside). After the extraction with ether was complete, acetone extracted amorphous, reddish-brown *sennaisoemodin*, $C_{15}H_{10}O_5$, soluble in light petroleum, together with senna-rhamnetin, which is insoluble in this solvent; there remained undissolved black, amorphous *sennanigrin* (C 60.5, H 5.0 per cent. approximately), which yields senna-emodin and sennachrysophanic acid when hydrolysed with boiling alcoholic potash, and chrysammic acid when boiled with nitric acid. It seems better to extract the leaves with 60 per cent. alcohol instead of with dilute ammonia.

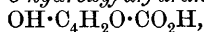
As the purgative action of the drug appears due to the hydroxymethylantranthraquinone derivatives, the amount of these was estimated by a spectroscopic method; it was greatest in the fruits, but even then much less than in *Rheum* and *Frangula*; as regards the leaves, Alexandria senna contained the largest amount, Tinnevely the smallest.

C. F. B.

Colouring Matter of Saffron. By ALBERT HILGER (*Chem. Centr.*, 1900, ii, 576; from *Verh. Vers. Deutsch. Naturf. Aerzte*, 1899, 669).—The colouring matter of saffron is a phytostearyl ester of palmitic and stearic acids and contains also a hydrocarbon, C_nH_{2n+2} , which melts at 71° . In the living stigma, it is combined with glucose and an ethereal oil. The oil consists of terpene and a compound, $C_{10}H_{18}O$. The fractions of lower boiling points contain pinene and cineol.

E. W. W.

Interaction of Furfuraldehyde and Caro's Reagent. By CHARLES F. CROSS, EDWARD J. BEVAN, and JOHN F. BRIGGS (*Chem. News*, 1900, 82, 163).—With hydrogen peroxide, furfuraldehyde forms 3:2-hydroxyfurfuraldehyde and a small quantity of the corresponding acid (*Trans.*, 1899, 75, 749); with Caro's reagent, it yields what appears to be 5-hydroxyfurfuran-2-carboxylic acid,



which forms soluble lead and barium salts, gives a yellowish-red precipitate with ferric chloride like the isomeric pyromucic acid, is readily

hydrolysed, and when boiled in a solution kept at constant volume is decomposed yielding formic acid; hydrolysis also occurs on attempting to isolate the barium and calcium salts, with the production of a dibasic acid. By reduction with sodium amalgam, a hydroxyfurfuraldehyde is produced which differs from the others previously obtained.

Caro's reagent does not attack dextrin, but oxidises lævulose slowly; it also oxidises the hydroxyfurfuraldehyde of the ligno-celluloses; hence it differs from the ordinary oxidising agents used in bleaching.

D. A. L.

Composition of Berberine Phosphate. By FRANK SHEDDEN (*Pharm. J.*, 1900, [iv], 11, 89—90).—Berberine phosphate, $C_{20}H_{17}O_4N, 2H_3PO_4, 1\frac{1}{2}H_2O$, prepared by adding excess of phosphoric acid to berberine-acetone, is a bright yellow, non-deliquescent crystalline substance soluble in 14.3 parts of water at 16° . The dehydrated salt dissolves in 15 parts of water at $15-16^\circ$. When prepared by Parsons and Wrampelmeier's method (*Proc. Amer. Pharm. Assoc.*, 1879, 514) it contains $1H_2O$.

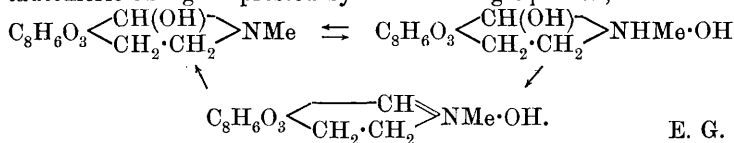
Estimation of berberine in its salts by conversion to the chloroform compound gives low results.

R. L. J.

The Alkaloids of Ceanothus Americanus. By HARRY M. GORDIN (*Pharm. Rev.*, 1900, 18, 266—268).—From an alcoholic solution of Gerlach's ceanothine (*Amer. J. Pharm.*, 63, 332) two fractions may be obtained, one of which melts at 255° and, like its picrate, dissolves sparingly in alcohol, the other melts at 200° and is easily soluble in alcohol, as also is its picrate.

R. L. J.

Some Ammonium Compounds. VI. Formula of Cotarnine. By HERMAN DECKER (*Ber.*, 1900, 33, 2273—2274).—Hantzsch and Kalb (this vol., i, 113) have suggested that solutions of cotarnine contain a compound, $C_8H_6O_3 \langle \begin{smallmatrix} CH(OH) \\ CH_2 \cdot CH_2 \end{smallmatrix} \rangle NMe$, which they have termed pseudocotarnine. This formula was first proposed for cotarnine by the author (*J. pr. Chem.*, 1893, [ii], 47, 223), who considers that the abnormal conductivity of cotarnine solutions cannot be explained by the hypothesis of Hantzsch and Kalb, but is dependent on a tautomeric change expressed by the following equation,



E. G.

Poisonous Boraginæ Alkaloids. By KARL GREIMER (*Arch. Pharm.*, 1900, 238, 505—531).—*Cynoglossum offic.*, *Anchusa offic.*, and *Echium vulgare* contain an alkaloid, *cynoglossine*, of which the hydrochloride is crystalline and forms crystalline double compounds with mercuric chloride and platinic chloride (the latter in crystals of the regular system, with C 18.6, H 4.4, Pt 32.6); these were utilised in the purification of the alkaloid. The physiological action of cynoglossine is to paralyse the peripheral nerve terminations.

Symphytum offic. contains an alkaloid, *symphytocynoglossine*, which

in its chemical behaviour exhibits no difference from cynoglossine, but has a different physiological action; it paralyses the central nervous system.

In addition to cynoglossine and symphytocynoglossine the plants in question contain choline, which seems to be present in particularly large amount in the dried roots.

These four *Boraginæ* contain a glucoside, *consolidin*, which has also the properties of an alkaloid, and is decomposed by acids into glucose and consolicine. It paralyses the central nervous system.

Consolicine, the product of the decomposition of *consolidin*, is also an alkaloid, and is present as such in the four plants examined. It paralyses the central nervous system (with the exception, possibly, of the specimen from *Anchusa offic.*) and its action is three times as strong as that of *consolidin*. Its hydrochloride was obtained in the crystalline state. C. F. B.

Cytisine and some of its Alkyl Derivatives. By A. RAUWERDA (*Arch. Pharm.*, 1900, 238, 477—486).—Cytisine was extracted from the seeds of *Cytisus laburnum*, L., by percolation with 80 per cent. alcohol and treatment of the extracted substance with chloroform, and was purified by distillation under 2 mm. pressure. It forms rhombic crystals [$a:b:c=0.6768:1:0.5574$]. Methylcytisine crystallises from absolute alcohol in hemihedral rhombic needles [$a:b:c=0.7973:1:0.9632$], from water with $2H_2O$ in rhombic crystals [$a:b:c=0.6156:1:1.8572$]. Determinations of the solubility and optical rotation of these two substances, in various solvents, are given. *Ethylcytisine* was only obtained as an oil. *Cetylcytisine* was obtained by heating powdered cytisine with cetyl iodide at 100° ; it melts at $55-56^\circ$, and has the specific rotation $[\alpha]_D$ 112° in chloroform and $122.40'$ in methyl alcohol solution. C. F. B.

Damascenine, a Constituent of the Seeds of Nigella Damascena, L. By HERBERT POMMERHNE (*Arch. Pharm.*, 1900, 238, 531—555. Compare Abstr., 1899, i, 964, and Schneider, *Pharm. Centralh.*, 1890, 173).—The formula $C_9H_{11}O_3N$ is now assigned to damascenine, from new analyses of the alkaloid and its salts; it contains only one and not two methoxyl groups. The following salts are described, with their formulæ and melting points. ($A=C_9H_{11}O_3N$).—Hydrochloride, A, HCl, H_2O , $194-197^\circ$. Hydrobromide, A, HBr , $197-199^\circ$; with $1H_2O$, $117-118^\circ$; with $2H_2O$, $104-106^\circ$. Hydroiodide, A, HI , $168-169^\circ$; with $2H_2O$ $112-115^\circ$. Nitrate, A, HNO_3 , 180° ; with $2H_2O$, $93-95^\circ$. Sulphates, $2A, H_2SO_4$, $183-185^\circ$; A, H_2SO_4 , $203-205^\circ$. Picrate, $A, C_6H_3O_7N_3$, $189-190^\circ$. Platinichloride, $2A, H_2PtCl_6, 4H_2O$, $197-198^\circ$.

Damascenine, obtained from the hydrochloride by treatment with aqueous sodium carbonate and extraction with ether, melts at 26° . The yield is small, as a large part appears to undergo a molecular transformation, under the influence of the alkali, into a substance which is insoluble in ether, but forms salts identical, or nearly so, in composition and properties, with those of damascenine itself. Alcoholic potash effects the same transformation; the methoxyl group is not removed.

Damascenine unites with 1 mol. of methyl iodide in methyl alcoholic solution at 100°; from the product several other salts were prepared. *Methiodide*, $A, MeI, 2H_2O$, 168—170°. *Methochloride platinichloride*, $(A, Me)_2PtCl_6$, 181—183°; *aurichloride*, $(A, Me)AuCl_4$, 153—155°, *mercurichloride*, $(A, Me)HgCl_2$, 158—160°. *Methonitrate*, 120—121°.

C. F. B.

Laudanosine. By AMÉ PICTET and B. ATHANASESCU (*Ber.*, 1900, 33, 2346—2353).—Laudanosine, one of the more obscure opium alkaloids, is identical with *d-N*-methyltetrahydropapaverine, prepared by reducing papaverine methochloride and splitting the product with quinic acid; its constitution is therefore represented by the formula

$$\begin{array}{ccccccc} OMe \cdot C \cdot CH \cdot C \cdot CH_2 \cdot CH_2 \cdot NMe & & CH \cdot C(OMe) \cdot C \cdot OMe \\ | & & | \\ OMe \cdot C \cdot CH \cdot C & \text{---} & CH \cdot CH_2 \cdot C \cdot CH & \text{---} & CH \end{array}$$

Racemic N-methyltetrahydropapaverine crystallises from dilute alcohol or light petroleum in long, white needles melting at 115°, and dissolves to some extent in boiling water; the alcoholic solution is strongly alkaline and has a bitter taste. With the usual reagents, the alkaloid develops colorations identical with those which characterise laudanosine. The *platinichloride*, *mercurichloride*, and *picrate* melt at 160°, 172°, and 174° respectively; the *methiodide* and *ethiodide* form large crystals melting at 215—217° and 202—203° respectively. The base is more poisonous than papaverine, its toxic properties being comparable with those of thebaine; laudanosine also approaches thebaine in this respect, but unlike papaverine does not exert a narcotic effect.

M. O. F.

Inactive Nicotine. By AMÉ PICTET and A. ROTSCHY (*Ber.*, 1900, 33, 2353—2355).—By heating aqueous solutions of nicotine monohydrochloride or sulphate in sealed tubes at 180—250° during periods varying according to the temperature and the nature of the salt, an inactive mixture of the antipodes has been obtained.

M. O. F.

Reduction of Nicotyrine to Inactive Nicotine. By AMÉ PICTET (*Ber.*, 1900, 33, 2355—2356).—When dihydronicotyrine (*Abstr.*, 1898, i, 588), dissolved in glacial acetic acid is treated with bromine in the same solvent, a pale yellow, crystalline substance is produced which, on reduction with tin and hydrochloric acid, yields inactive nicotine.

M. O. F.

Pilocarpine. By ADOLF PINNER and ERICH KOHLHAMMER (*Ber.*, 1900, 33, 2357—2363. Compare this vol., i, 456, and Jowett, *Trans.*, 1900, 77, 494, 851).—When pilocarpine is oxidised with potassium permanganate, all the nitrogen is eliminated, one half being converted into ammonia, the remainder disappearing in the form of methylamine; the dibasic acid, $C_8H_{14}O_6$, obtained in this way (compare, however, Jowett, *loc. cit.*, 855, and following abstract) is also produced when the alkaloid is oxidised with hydrogen peroxide. Chromic acid, however, gives rise to the dibasic acid, $C_{11}H_{16}O_5N_2$.

Piluvic acid, $C_8H_{14}O_6$, prepared by oxidising a 5 per cent. solution of pilocarpine with 0.5 per cent. potassium permanganate solution, yields the amorphous *silver* salt, which is very sensitive to light and

heat; the *potassium* salt is hygroscopic, and loses H_2O at 100° , yielding the *potassium* salt of the acid $\text{C}_8\text{H}_{12}\text{O}_5$, of which the *ethyl* ester boils at 181 — 183° and 293° under pressures of 26 mm. and 755 mm. respectively. The *barium* salt, $\text{C}_8\text{H}_{12}\text{O}_6\text{Ba}$, is a white, amorphous powder, which loses no water at 110° , and only $\frac{1}{2}\text{H}_2\text{O}$ at 180° .

Pilocarpoeic acid, $\text{C}_{11}\text{H}_{16}\text{O}_5\text{N}_2$, formed when pilocarpine dissolved in dilute sulphuric acid is oxidised with chromic acid, is a colourless gum, which melts below 100° , and dissolves very readily in water; the *barium* salt is amorphous, and only slightly hygroscopic.

M. O. F.

Constitution of Pilocarpine. By HOOPER A. D. JOWETT (*Ber.*, 1900, 33, 2892—2895. Compare preceding abstract).—Pinner and Kohlhammer's ethyl piluvate, $\text{C}_8\text{H}_{10}\text{O}_5\text{Et}_2$, boiling at 293° , is identical with the ester boiling at 299° , to which the author assigned the formula $\text{C}_9\text{H}_{14}\text{O}_4$. The accuracy of the latter formula, and of the view that the substance is the monoethyl ester of a monobasic lactonic acid is maintained.

T. M. L.

The Alkaloids of *Bocconia* (Macleya) cordata. By PAUL MURRILL and J. O. SCHLOTTERBECK (*Pharm. J.*, 1900, [iv], 11, 34—35; *Ber.*, 1900, 33, 2802—2807. Compare Eijkmann, *Abstr.*, 1885, 404; Hopfgartner, *Abstr.*, 1898, i, 606).—From *Bocconia cordata*, the tree celandine of the United States, the following alkaloids have been isolated. Protopine (macleyine), $\text{C}_{20}\text{H}_{19}\text{O}_5\text{N}$, forming about two-thirds of the alkaloidal yield, melting point 208° (corr.); β -homochelidonine, $\text{C}_{21}\text{H}_{21}\text{O}_5\text{N}$, forming about one-third of the yield, melting point 158.5° (corr.); and chelerythrine, which occurs only in very small quantity. The fluorescence of solutions of chelerythrine (compare Schmidt, Koenig and Tietz, *Abstr.*, 1893, i, 490), disappears with increased purity of the substance. Sanguinarine was not isolated, and was recognised only by the blood-red colour of its salts.

R. L. J.

Syntheses in the Animal Organism. I. Piperidine Derivatives. By HERMANN HILDEBRANDT (*Chem. Centr.*, 1900, ii, 202—203).—See this vol., ii, 676.

Action of Bromoacetophenone on Piperidine. By ERNST SCHMIDT and H. HARTONG VAN ARK (*Arch. Pharm.*, 1900, 238, 330—334).—When bromoacetone is allowed to remain with piperidine, best at the ordinary temperature and in ethereal solution, the *piperidylacetophenone bromide*, $\text{CPhO}\cdot\text{CH}_2\cdot\text{C}_5\text{NH}_{10}$, HBr , is obtained. This melts at 220° ; the corresponding *platinichloride* and *aurichloride* at 204 — 205° and 153 — 154° respectively. The base was isolated as an oily liquid; it forms a *methiodide*, $\text{CPhO}\cdot\text{CH}_2\cdot\text{C}_5\text{H}_{10}\text{N}$, MeI , melting at 185° , from which an *aurichloride* and a *platinichloride*, melting respectively at 129 — 130° and 222° , and a syrupy, alkaline hydroxide were prepared. The hydroxide was submitted to dry distillation, but only piperidine and methylpiperidine could be identified amongst the products.

The mother liquor from the piperidylacetophenone contains *piperidiodiacetophenone bromide*, $\text{C}_5\text{NH}_{10}\text{Br}(\text{CH}_2\cdot\text{CPhO})_2$, H_2O ; this melts when anhydrous at 164° , the corresponding *platinichloride* at 205° .

C. F. B.

Action of Cyanogen Bromide on Tertiary Amines. III. By JULIUS VON BRAUN (*Ber.*, 1900, **33**, 2734—2736. Compare this vol., i, 641).—When cyanogen bromide reacts with methylpiperidine in ethereal solution, an unstable intermediate product is produced which decomposes into dimethylpiperidinium bromide and cyanopiperidine.
G. T. M.

Thiazolines and Oxazolines. By FRITZ SAULMANN (*Ber.*, 1900, **33**, 2634—2639. Compare Gabriel, *Abstr.*, 1890, 524; 1891, 701;

1892, 1331; 1897, i, 120).—2- β -Naphthylthiazoline, $\begin{array}{c} \text{CH}_2\text{-S} \\ | \\ \text{CH}_2\text{-N} \end{array} \gg \text{C}\cdot\text{C}_{10}\text{H}_7$, obtained from β -naphthoylthiamide and ethylene bromide or bromoethylamine hydrobromide, is a colourless compound melting at 80° and readily soluble in the usual organic solvents. The *hydrobromide*, $\text{C}_{13}\text{H}_{12}\text{NSBr}$, has a pale yellow colour, melts at 213° , and is sparingly soluble in water; the *platinichloride* melts at 218° . 2- α -Naphthylthiazoline is an oil, the *picrate* of which forms yellow crystals melting at

162° . 2- α -Naphthyl-5-methylthiazoline, $\begin{array}{c} \text{CHMe}\cdot\text{S} \\ | \\ \text{CH}_2\text{-N} \end{array} \gg \text{C}\cdot\text{C}_{10}\text{H}_7$, obtained from α -naphthoylthiamide and β -bromopropylamine hydrobromide, is also an oil. 2- β -Naphthylpenthiiazoline, $\text{CH}_2\text{-} \begin{array}{c} \text{CH}_2\text{-S} \\ \text{CH}_2\text{-N} \end{array} \gg \text{C}\cdot\text{C}_{10}\text{H}_7$, obtained by the aid of trimethylene chlorobromide, melts at 82° , and its *picrate*, which is insoluble in water, at 169° . The isomeric α -compound melts at 103° , and its *hydrochloride* decomposes at 260° .

p-Bromobenzoylthiamide, obtained from *p*-bromobenzonitrile and alcoholic ammonium sulphide, crystallises in yellow prisms melting at 145° , and when heated with ethylene bromide yields 2-*p*-bromophenylthiazoline, which crystallises in long needles melting at 88° ; the *picrate* melts at 202° , and the *platinichloride* decomposes at 217° . 2-*p*-Bromophenyl-5-methylthiazoline, is an oil, and its *picrate* melts at 182° .

β -Naphthoylbromoethylamide, $\text{C}_{10}\text{H}_7\cdot\text{CO}\cdot\text{NH}\cdot\text{C}_2\text{H}_4\text{Br}$, crystallised from toluene, melts at 152° , and when treated with alcoholic potash yields 2- β -naphthylloxazoline, $\begin{array}{c} \text{CH}_2\cdot\text{O} \\ | \\ \text{CH}_2\text{-N} \end{array} \gg \text{C}\cdot\text{C}_{10}\text{H}_7$, as an oil.

α -Naphthoylbromoethylamide melts at 97° , and 2- α -naphthylloxazoline at 50° ; the *dichromates* of both bases are unstable. β -Naphthoyl- β -bromopropylamide is sparingly soluble in ether and yields 2- β -naphthyl-5-methylloxazoline in the form of a syrup, the *picrate* of which melts at 197° , and the *platinichloride* at 209° . α -Naphthoyl- β -bromopropylamide crystallises in felted needles and melts at 100° ; 2- α -naphthyl-5-methylloxazoline is an oil which forms a *picrate* melting at 170° and a *platinichloride* melting at 197° .
J. J. S.

Action of Bromoacetophenone on Pyridine. By ERNST SCHMIDT and H. HARTONG VAN ARK (*Arch. Pharm.*, 1900, **238**, 321—330. Compare Rumpel, *Abstr.*, 1898, i, 246, &c.).—From pyridineacetophenone (pyridinephenacyl) bromide, $\text{CPhO}\cdot\text{CH}_2\cdot\text{C}_5\text{NH}_5\text{Br}$, melting at

198°, the corresponding *chloride* (with $1\text{H}_2\text{O}$) *platinichloride*, *aurichloride*, and *mercurochloride*, $\text{C}_{13}\text{H}_{12}\text{ONCl}\cdot\text{HgCl}_2$, were prepared; these melt at 196—198°, 229—231°, 174°, and 189° respectively. The bromide is hydrolysed to benzoic acid and methylpyridine by warming with 5 per cent. aqueous sodium carbonate; when reduced with zinc dust and hydrochloric acid, it yields pyridine and apparently acetophenone. The chloride forms an *oxime*, $\text{NOH}\cdot\text{CPh}\cdot\text{CH}_2\cdot\text{C}_5\text{NH}_5\text{Cl}$, melting at 210°, from which a *platinichloride* and an *aurichloride*, melting at 196—198° and 136° respectively were prepared. The oxime chloride is not affected by boiling with acetyl chloride or with acetic anhydride and anhydrous sodium acetate; when heated in the water-bath with acetyl or benzoyl chloride, or at 150° with fuming hydrochloric acid, it is hydrolysed to hydroxylamine and pyridineacetophenone chloride; when heated for a short time at 100° with strong sulphuric acid, it yields a substance, $\text{C}_{13}\text{H}_{12}\text{O}_4\text{N}_2\text{S}\cdot\frac{1}{2}\text{H}_2\text{O}$, apparently of the nature of a sulphonic acid, together with hydroxylamine and pyridineacetophenone sulphate; when allowed to remain with a mixture of phosphorus pentachloride and oxychloride, it forms a compound, possibly $\text{NHPh}\cdot\text{CO}\cdot\text{CH}_2\cdot\text{C}_5\text{NH}_5\text{Cl}$, of which the *aurichloride* and *platinichloride* melt at 180° and 210—213° respectively. Attempts to reduce the oxime chloride to an amine in dilute acetic acid solution with sodium amalgam were unsuccessful. C. F. B.

Additive Compounds formed by Nitriles with Tripyridinechromium Trichloride: Dithiocyanodiethylenediaminechromium Salts. By PAUL PFEIFFER (*Ber.*, 1900, 33, 2686—2691).—The *additive compound*, $\text{Cr}_3(\text{C}_5\text{NH}_5)_3\text{Cl}_3\cdot 2\text{MeCN}$, separates rapidly from a solution of tripyridinechromium trichloride in acetonitrile in bright-green, microscopic rhombic plates. With propionitrile, the *compound* $\text{Cr}_3(\text{C}_5\text{NH}_5)_3\text{Cl}_3\cdot\text{EtCN}$ appears to be formed, the composition of which varies on keeping; with benzonitrile a similar compound is obtained. Attempts to obtain analogous derivatives from dipyridinecupric chloride, $\text{Cu}(\text{C}_5\text{NH}_5)_2\text{Cl}_2$, and dipyridinezinc chloride failed.

On heating triethylenediaminechromium thiocyanate (this vol., i, 559) at 120—130°, it loses 1 mol. of ethylenediamine and yields *dithiocyanodiethylenediaminechromium thiocyanate* $[\text{Cr}(\text{C}_2\text{H}_8\text{N}_2)_2(\text{SCN})_2]\text{SCN}\cdot 2\text{H}_2\text{O}$, which crystallises from water in long, flat, lustrous, orange-yellow needles, and forms acid salts with concentrated hydrochloric and hydrobromic acids. With warm dilute sulphuric acid, the *salt* $[\text{Cr}(\text{C}_2\text{H}_8\text{N}_2)_2(\text{SCN})_2]\text{SO}_4\cdot 2\text{H}_2\text{O}$, is obtained in long, transparent, efflorescent, orange prisms. Since the foregoing thiocyanate gives a normal reaction with ferric salts and the derived sulphate fails to do so, the author assumes the existence of the radicle $[\text{Cr}(\text{C}_2\text{H}_8\text{N}_2)_2(\text{SCN})_2]$ in the latter; the salts thus belong to the type $(\text{MA}_4\text{X}_2)\text{X}$, of Werner's classification of additive compounds of amines with metallic salts. W. A. D.

Luminosity of 1-Ethyl-2-quinolone. By HERMAN DECKER (*Ber.*, 1900, 33, 2277—2278).—When large crystals of ethylquinolone are crushed, they emit a bluish light similar to that of the electric spark;

this effect is not produced by any other of many quinolone derivatives examined. E. G.

Some Ammonium Compounds. VII. The Nitration of Alkyl-Quinoline Salts. By HERMAN DECKER (*Ber.*, 1900, 33, 2275—2277).—When ethylquinoline nitrate is left for a few hours in the cold with excess of nitrosulphuric acid, and the nitroethylquinoline so formed is liberated with alkali and oxidised by means of potassium ferricyanide, 5-nitro-1-ethyl-2-quinolone is produced. This method for the preparation of nitro-2-quinolones is much simpler than that previously described by the author (*Abstr.*, 1892, 879). E. G.

Transformations of Phthaliminoketones. By SIEGMUND GABRIEL and JAMES COLMAN (*Ber.*, 1900, 33, 2630—2634. Compare this vol., i, 358).—Benzylphthalimide undergoes no transformation in the presence of sodium ethoxide, whereas acetonylphthalimide and phenacylphthalimide are readily converted into isocarbostyryl derivatives. 3-Acetyl-4-hydroxyisocarbostyryl, $\text{C}_6\text{H}_4 \begin{smallmatrix} \text{CO} \text{---} \text{NH} \\ \diagup \quad \diagdown \\ \text{C}(\text{OH}) \text{:} \text{C} \text{Ac} \end{smallmatrix}$ crystallises in colourless needles melting at about 270° , yields a *phenylhydrazone* crystallising in lemon-yellow, six-sided plates and decomposing at 250° , and, when reduced with hydriodic acid and red phosphorus, yields isocarbostyryl; an isomeric *acetyl* derivative melting at $207\text{--}208^\circ$ is obtained by the action of acetic anhydride on 4-hydroxyisocarbostyryl. 3-Benzoyl-4-hydroxyisocarbostyryl crystallises from alcohol in yellow, hair-like needles melting at $196\text{--}198^\circ$. J. J. S.

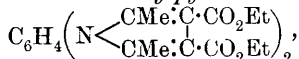
Aminonaphthacridinium Compounds. By FRITZ ULLMANN and E. NAEF (*Ber.*, 1900, 33, 2470—2475).—The monoacetyl derivative of “aminomethylnaphthacridine” (this vol., i, 361, where also see footnote as to nomenclature) forms the yellow iodide of “3'-acetyl-amino-2':10-dimethyl-1:2-naphthacridinium,” when it is heated at $140\text{--}150^\circ$ with methyl iodide and chloroform. The methylation is more easily effected by dissolving the acridine in nitrobenzene, and adding freshly distilled dimethyl sulphate to the solution at $150\text{--}160^\circ$; the *acridinium methyl sulphate*, $\text{C}_{10}\text{H}_{16} \begin{smallmatrix} \text{CH} \\ \diagup \quad \diagdown \\ \text{NMe}(\text{MeSO}_4) \end{smallmatrix} \text{C}_6\text{H}_2\text{Me} \cdot \text{NHAc}$, crystallises out at once as a yellow powder. The acetyl group can be removed by boiling with dilute hydrochloric acid; from the solution, potassium nitrate precipitates red “aminodimethylnaphthacridinium” *nitrate*, which melts and decomposes at $286\text{--}290^\circ$; from a dilute boiling solution of the nitrate, potassium dichromate precipitates the red *dichromate*; when dimethyl sulphate is used, there is no need to employ the acetyl-amino-compound; the aminoacridine itself can be methylated directly, the acridinium methyl sulphate separating in red crystals.

Ethyl bromide reacts with the acetyl-amino-compound rather less readily than methyl iodide does; the product, “3'-acetyl-amino-2'-methyl-10-ethyl-1:2-naphthacridinium” *bromide*, forms yellow crystals and melts at $265\text{--}269^\circ$. The acetyl group can be removed by boiling with hydrobromic acid; the resulting “aminomethylethylnaphth-

acridinium" bromide forms red crystals, and melts and decomposes at 298°. C. F. B.

Difference of Basicity of the two Amino-groups of Substituted Diamines. I. *m*-Tolylenediamine. By CARL BÜLOW (*Ber.*, 1900, 33, 2364—2370).—Tiemann observed (*Ber.*, 1870, 3, 221) that when *m*-tolylenediamine (1-methyl-2:4-diaminobenzene) is heated with slightly less than 2 mols. of glacial acetic acid and a very small quantity of water, it is the *p*-amino-group almost exclusively which is acetylated; similarly, Koch has shown (*Annalen*, 1870, 153, 132) that the diacetyl derivative is converted entirely into the 2-amino-4-acetamino-derivative when heated with 1 mol. of sodium hydroxide. The author finds that the same principle, namely, the greater reactivity of the 4-amino-group, underlies the condensation of *m*-tolylenediamine with ethyl diacetylsuccinate.

Ethyl p-phenylene-bis-2:5-dimethylpyrrole-3:4-dicarboxylate,



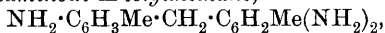
prepared by heating *p*-phenylenediamine with ethyl diacetylsuccinate in glacial acetic acid, crystallises from dilute alcohol in white scales melting at 172—173°.

Ethyl 1-o-acetylamino-p-tolyl-2:5-dimethylpyrrole-3:4-dicarboxylate,

$\text{NHAc} \cdot \text{C}_6\text{H}_3\text{Me} \cdot \text{N} \begin{array}{l} \text{CMe} \cdot \text{C} \cdot \text{CO}_2\text{Et} \\ \text{CMe} \cdot \text{C} \cdot \text{CO}_2\text{Et} \end{array}$, obtained from *o*-acetyl-*m*-tolylene-

diamine and ethyl diacetylsuccinate, crystallises in white needles melting at 120—121°. *Ethyl 1-p-acetylamino-o-tolyl-2:5-dimethylpyrrole-3:4-dicarboxylate*, $\text{C}_{21}\text{H}_{26}\text{O}_5\text{N}_2$, prepared from *p*-acetyl-*m*-tolylenediamine and ethyl diacetosuccinate, melts at 160°. It is the former of these two substances which is produced on acetylating the condensation product of *m*-tolylenediamine and ethyldiacetosuccinate (*Annalen*, 1886, 236, 311. M. O. F.

Preparation of Diphenylmethane Derivatives from *p*- and *o*-Aminobenzylaniline and their Homologues. By PAUL COHN and ARMIN FISCHER (*Ber.*, 1900, 33, 2586—2592).—The methods employed for the preparation of the compounds described in the paper have formed the subject of the German Patent, 107718, but the compounds themselves have not been described. 4-Aminophenyl-4-amino-*m*-tolylmethane, $\text{NH}_2 \cdot \text{C}_6\text{H}_3\text{Me} \cdot \text{CH}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{NH}_2$, is formed by the action of hydrochloric acid on *o*-toluidine and *p*-aminobenzylaniline, and has already been described. 4-Aminophenyl-2:4-diamino-*m*-tolylmethane, $\text{C}_6\text{H}_2\text{Me}(\text{NH}_2)_2 \cdot \text{CH}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{NH}_2$, is obtained in a similar manner from *m*-tolylenediamine, and forms compact, yellowish crystals melting at 139—140°. *p*-Amino-*m*-xylyl-*p*-toluidine forms white crystals melting at 93—94°, and with *m*-tolylenediamine yields 4:2':4'-triaminodi-*m*-tolylmethane,



which crystallises in slender, yellowish needles melting at 163°.

p-Dimethylaminobenzyl-*p*-toluidine, $\text{NMe}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{CH}_2 \cdot \text{NH} \cdot \text{C}_6\text{H}_4\text{Me}$, is obtained by the action of anhydroformaldehyde-*p*-toluidine on a mixture of dimethylaniline and *p*-toluidine, and melts at 105—106°;

the *hydrochloride*, $C_{16}H_{20}N_2 \cdot 2HCl$, crystallises in white needles. With aniline, the base yields 4-amino-4'-dimethylaminodiphenylmethane, $NMe_2 \cdot C_6H_4 \cdot CH_2 \cdot C_6H_4 \cdot NH_2$, which melts at 90—91°; with *o*-toluidine, the same base yields 4-dimethylaminophenyl-4-amino-*m*-tolylmethane, $NMe_2 \cdot C_6H_4 \cdot CH_2 \cdot C_6H_3Me \cdot NH_2$, which crystallises in greyish-white, silky needles, melts at 92—93°, and with *m*-tolylenediamine yields the corresponding 4-dimethylaminophenyl-2':4'-diamino-*m*-tolylmethane, $NMe_2 \cdot C_6H_4 \cdot CH_2 \cdot C_6H_2Me(NH_2)_2$, which forms yellowish crystals and melts at 112—113°.

p-Diethylaminobenzyl-*p*-toluidine, $NEt_2 \cdot C_6H_4 \cdot CH_2 \cdot NH \cdot C_6H_4Me$, crystallises in long, white prisms melting at 59—60°. *o*-Amino-*m*-xylyl-*p*-toluidine, $NH_2 \cdot C_6H_3Me \cdot CH_2 \cdot NH \cdot C_6H_4Me$, crystallises in white plates melting at 87°, and its *hydrochloride* in short prisms. With *m*-tolylenediamine it yields 2:2':4'-triaminodi-*m*-tolylmethane, $NH_2 \cdot C_6H_3Me \cdot CH_2 \cdot C_6H_2Me(NH_2)_2$, melting at 154°. A. H.

4-Hydroxypyrazole and its Derivatives. By LUDWIG WOLFF (*Annalen*, 1900, 313, 1—24).—The three methods by which the author has obtained derivatives of 4-hydroxypyrazole are the following: (1) Tetric acid and benzenediazonium chloride yield the α -phenylhydrazone of diketobutylolactone (this vol., i, 584), which, when heated with sodium hydroxide, is transformed into 4-hydroxy-1-phenyl-

pyrazole-3-carboxylic acid, $NPh \begin{smallmatrix} CH:C:OH \\ | \\ N=C \end{smallmatrix} CO_2H$. (2) Ethyl γ -bromoacetoacetate combines with benzenediazonium chloride, forming a phenylhydrazone which loses hydrogen bromide under the influence of alkalis, becoming converted into the ethyl salt of the foregoing acid. (3) Sodium diazotetronosulphonate (*loc. cit.*), under the influence of sodium hydroxide, followed by hydrochloric acid, yields 4-hydroxypyrazole-3-carboxylic acid.

[With A. LÜTTINGHAUS].—4-Hydroxypyrazole-3-carboxylic acid, $NH \begin{smallmatrix} CH:C:OH \\ | \\ N=C \end{smallmatrix} CO_2H$, prepared by heating sodium diazotetronosulphonate with sodium hydroxide and adding cold dilute hydrochloric acid to the clear solution, crystallises from boiling water in aggregates of lustrous needles containing $1H_2O$ and melting at 204—205° when carbon dioxide is eliminated; the aqueous solution develops a bluish-violet coloration with ferric chloride and becomes yellowish-red with sodium nitrite. The *tribenzoyl* derivative, $C_{25}H_{16}O_6N_2$, crystallises from alcohol in slender needles and melts at 137°; the *benzoyl* derivative, $C_{11}H_8O_4N_2$, separates from dilute alcohol in aggregates and melts at 210—212°, evolving gas.

4-Hydroxypyrazole, $NH \begin{smallmatrix} CH:C:OH \\ | \\ N=CH \end{smallmatrix}$, obtained on eliminating carbon dioxide from the carboxylic acid, crystallises from chloroform in white plates and melts at 118—118.5°; the aqueous solution, which is very feebly acidic, develops a greenish-blue coloration with ferric chloride, becomes yellowish-green with sodium nitrite, and reduces solutions of mercuric chloride and silver nitrate. The *picrate* forms long, yellow needles, and melts at 128—129°; the *hydrochloride* melts at 157°, and the *platinichloride* dissolves very readily in water and in alcohol. The

dibenzoyl derivative, $C_{17}H_{12}O_3N_2$, crystallises from alcohol in long, white needles, and melts at 109° .

4-Hydroxy-1-methylpyrazole *methiodide*, $C_5H_9ON_2I$, prepared by heating 4-hydroxypyrazole with methyl iodide and methyl alcohol at 120° , crystallises from alcohol in plates melting at 141° ; the ammonium base crystallises in needles, which dissolve very readily in water, forming a strongly alkaline reducing solution, and the *platinichloride* crystallises in needles which decompose at 212° . 4-Hydroxy-1-methyl-

pyrazole, $NMe \begin{smallmatrix} CH:C\cdot OH \\ \diagdown \\ N=CH \end{smallmatrix}$, produced on heating the methiodide, crystallises from a mixture of chloroform and petroleum in white prisms and melts at 89° ; the hydrochloride is decomposed by water.

[With EDUARD FERTIG.]—The α -phenylhydrazone of ethyl γ -bromoacetoacetate, $NHPh\cdot N:C(CO_2Et)\cdot CO\cdot CHBr$, crystallises from dilute alcohol in yellow needles, and melts at 80 – 81° ; it is sparingly soluble in sodium carbonate, but dissolves readily in sodium hydroxide.

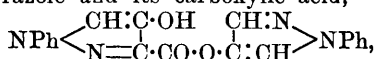
4-Hydroxy-1-phenylpyrazole-3-carboxylic acid, $NPh \begin{smallmatrix} CH:C\cdot OH \\ \diagdown \\ N=C\cdot CO_2H \end{smallmatrix}$, separates on adding hydrochloric acid to a solution of ethyl γ -bromoacetoacetate α -phenylhydrazone in hot sodium hydroxide, and crystallises from boiling water in needles which contain $\frac{1}{2}H_2O$ and melt at 130 – 140° ; the anhydrous compound crystallises from chloroform in large, lustrous prisms and melts at 153 – 154° . The acid develops a deep blue coloration with aqueous ferric chloride, and becomes yellow or red with sodium nitrite and hydrochloric acid, even in dilute solutions. The *silver* salt crystallises in needles, and the *ethyl* ester forms colourless plates which melt at 84 – 45° . The 5-phenylhydrazone of 1-phenyl-

4-keto-5-pyrazolone-3-carboxylic acid, $NPh \begin{smallmatrix} C(:N\cdot NPh)\cdot CO \\ \diagdown \\ N= \\ \diagup \\ C\cdot CO_2H \end{smallmatrix}$, obtained on adding sodium phenylhydroxypyrazolecarboxylate to freshly diazotised aniline, crystallises from dilute acetic acid in lustrous red needles which melt and evolve gas at 209° . 5-isoNitroso-1-phenyl-

4-ketopyrazoline-3-carboxylic acid, $NPh \begin{smallmatrix} C(:N\cdot OH)\cdot CO \\ \diagdown \\ N= \\ \diagup \\ C\cdot CO_2H \end{smallmatrix}$, formed on acidifying a solution of sodium phenylhydroxypyrazolecarboxylate and sodium nitrite, crystallises from dilute alcohol in bright red needles decomposing at 190 – 192° .

4-Hydroxy-1-phenylpyrazole, $NPh \begin{smallmatrix} CH:C\cdot OH \\ \diagdown \\ N=CH \end{smallmatrix}$, produced on eliminating carbon dioxide from hydroxyphenylpyrazolecarboxylic acid, crystallises from very dilute alcohol in long, white needles, melts at 119 – 120° , and boils at 335° under 736 mm. pressure, undergoing slight decomposition; it requires 570 parts of water at 25° , and 50–60 parts of boiling water to dissolve it, the aqueous solution becoming blue with ferric chloride and yellowish-red with sodium nitrite and acetic acid. The *hydrochloride* melts at 80° and loses hydrogen chloride in air; the *platinichloride* crystallises in orange-red prisms containing $5H_2O$ and melts at about 180° , when it evolves gas. The *benzoyl* derivative, $C_{16}H_{12}O_2N_2$, crystallises in colourless plates and melts at 78° , and the *phenylurethane*, $C_{16}H_{13}O_2N_3$, separates from

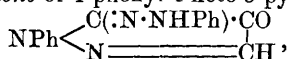
alcohol in long, white needles melting at 168°. The *anhydride* of phenylhydroxypyrazole and its carboxylic acid,



a bye-product in the preparation of hydroxyphenylpyrazole, crystallises from 80 per cent. alcohol in aggregates of lustrous needles melting at 177°; it is neutral towards sodium carbonate, and is resolved by hot sodium hydroxide into hydroxyphenylpyrazole and its carboxylic acid.

4-Chloro-1-phenylpyrazole, $\text{NPh} \left\langle \begin{array}{c} \text{CH:CCl} \\ \text{N}=\text{CH} \end{array} \right\rangle$, obtained on heating the hydroxy-compound with phosphorus oxychloride at 150° during 10 hours (compare Michaelis and Röhmer, *Abstr.*, 1899, i, 233), is identical with the compound prepared by Severini (*Abstr.*, 1894, i, 145) from 1-phenylpyrazole and sodium hypochlorite; it crystallises in long, silky needles and melts at 75–76°.

The 5-phenylhydrazone of 1-phenyl-4-keto-5-pyrazolone,



prepared by adding benzenediazonium chloride to the sodium derivative of hydroxyphenylpyrazole, crystallises from hot dilute acetic acid in lustrous, bronze-coloured needles melting at 122–125°. 5-iso-Nitroso-

1-phenyl-4-ketopyrazoline, $\text{NPh} \left\langle \begin{array}{c} \text{C}(\text{N}\cdot\text{OH})\cdot\text{CO} \\ \text{N}=\text{CH} \end{array} \right\rangle$, formed on adding acetic acid to a solution of hydroxyphenylpyrazole and sodium nitrite in dilute sodium hydroxide, crystallises from dilute alcohol in dark red prisms containing 1H₂O, and melts at 119–120°, slowly evolving gas.

4-Hydroxy-1-phenylpyrazole *methiodide*, C₁₀H₁₁ON₂I, crystallises from hot alcohol in long, white needles decomposing at 195°, when methyl iodide is eliminated; the ammonium *base*, C₁₀H₁₂O₂N₂, forms lustrous prisms which darken at 120° and melt at 132–135°. The *hydrochloride* crystallises in prisms decomposing at 203°, and the *platinichloride* forms yellow leaflets or prisms containing 2H₂O, and melts, evolving gas, at 193°. M. O. F.

5-Chloro- and 5-Bromo-1-phenyl-3-methylpyrazoles. By AUGUST MICHAELIS and HEINRICH BEHN (*Ber.*, 1900, 33, 2595–2607. Compare *Abstr.*, 1899, i, 233 and 941).—Phosphorus oxychloride and phenylmethylpyrazolone readily react when heated in a reflux apparatus, and the conversion of 5-chloro-1-phenyl-3-methylpyrazole into anti-pyrine takes place most readily in alcoholic solution.

When 5-chloro-1-phenyl-3-methylpyrazole is dissolved in fuming nitric acid, the product is a mixture of the mono- and di-nitro-derivatives, but with concentrated nitric acid (1 mol.) and sulphuric acid the mononitro-compound alone is formed. 5-Chloro-1-p-nitrophenyl-3-methylpyrazole crystallises in long, thin needles melting at 101°, and is readily soluble in organic solvents and also in concentrated hydrochloric acid; when brominated in ethereal solution, it yields 5-chloro-4-bromo-1-p-nitrophenyl-3-methylpyrazole, which crystallises in colourless

needles melting at 152.5° ; the same compound is obtained when 5-chloro-4-bromo-1-phenyl-3-methylpyrazole is nitrated, and hence the nitro-group must be in the benzene nucleus; that it occupies the *p*-position has been proved by direct synthesis from Altschul's *p*-nitrophenylmethylpyrazolone (Abstr., 1892, 1082) and phosphorus oxychloride. When heated at 125° for 6 hours with methyl iodide,

it yields the *methiodide*, $\begin{array}{c} \text{CH}=\text{CI} \\ | \\ \text{CMe:N(MeI)} \end{array} > \text{N} \cdot \text{C}_6\text{H}_4 \cdot \text{NO}_2$, which crystallises in glistening, yellow plates melting and decomposing at 229° . 1-*m*-Nitrophenyl-3-methylpyrazolone, obtained by heating ethyl acetoacetate *m*-nitrophenylhydrazone (Abstr., 1890, 150) at 140 – 150° , forms a yellow, crystalline powder insoluble in water or ether, and on treatment with phosphorus oxychloride is converted into 5-chloro-1-*m*-nitrophenyl-3-methylpyrazole melting at 103° and yielding a bromo-derivative which melts at 170° . 1-*o*-Nitrophenyl-3-methylpyrazolone crystallises in orange-red needles melting at 51° , the corresponding 5-chloro-pyrazole melts at 105.5° and yields a bromo-derivative melting at 123° .

5-Chloro-1-*o*-*p*-dinitrophenyl-3-methylpyrazole crystallises from toluene in yellow needles, melts at 181° , and is insoluble in concentrated hydrochloric acid; when reduced and treated with nitrous acid, it yields a dye similar to Bismarck brown and with *p*-phenylenediamine it gives an intense tolylene-blue.

5-Chloro-1-*p*-aminophenyl-3-methylpyrazole crystallises from alcohol in glistening plates containing $1\text{H}_2\text{O}$; it sinters at 62° and melts at 76 – 78° ; its acetyl derivative, $\begin{array}{c} \text{CH:CCl} \\ | \\ \text{CMe=N} \end{array} > \text{N} \cdot \text{C}_6\text{H}_4 \cdot \text{NHAc}, 2\text{H}_2\text{O}$, loses its

water at 80 – 85° and yields a *methiodide* melting at 171° . 5-Chloro-1-*p*-hydroxyphenyl-3-methylpyrazole crystallises from alcohol in glistening, yellow plates melting at 145.5° . 5-Bromo-1-phenyl-3-methylpyrazole, obtained by the action of phosphorus oxybromide at 125° , or of the tribromide at 140 – 150° , on phenylmethylpyrazolone, is an oily liquid distilling at 153° under 15 mm., or at 287° under atmospheric pressure; it has a sp. gr. 1.4408 at 8° ; its *methiodide*, $\text{C}_{10}\text{H}_9\text{N}_2\text{Br} \cdot \text{MeI}$, forms colourless needles melting at 233° , and yields a *periodide*, $\text{C}_{11}\text{H}_{12}\text{N}_2\text{BrI}_5$, melting at 57° ; its *methobromide* melts and decomposes at 218° , and yields a *perbromide*, $\text{C}_{11}\text{H}_{12}\text{N}_2\text{Br}_4$, melting at 146° ; the *methochloride* is very hygroscopic and melts at 214° . All three compounds, when treated with alcoholic potash or silver oxide, yield antipyrine. 4:5-Dibromo-1-phenyl-3-methylpyrazole, obtained as a bye-product in the preparation of the monobromo-compound, forms colourless, glistening plates melting at 92° , and is readily soluble in organic solvents or in concentrated hydrochloric acid.

5-Bromo-1-nitrophenyl-3-methylpyrazole crystallises in long needles, melts at 104.5° and is soluble in concentrated hydrochloric acid; the *dinitro*-derivative, which is insoluble in this acid, melts at 185.5° .

Both bromo- and chloro-phenylmethylpyrazoles, when reduced with zinc dust and hydrochloric acid, yield phenylmethylpyrazole melting at 36.5° , although with the chloro-compound the reduction is never complete. When phenylmethylpyrazole is brominated, the product is

4-bromo-1-phenyl-3-methylpyrazole, which is an oil distilling at 311—313° and having a sp. gr. 1.4575 at 8°; when further brominated, it yields the dibromo-derivative melting at 92°.

J. J. S.

1-*p*-Bromophenyl-3-methyl-5-chloropyrazole. By AUGUST MICHAELIS and G. SCHWABE (*Ber.*, 1900, 33, 2607—2614).—1-*p*-Bromophenyl-3-methylpyrazolone, obtained from *p*-bromophenylhydrazine and ethyl acetoacetate, forms colourless crystals melting at 175°; it readily condenses with aldehydes, yielding sparingly soluble, coloured compounds; the 4-benzylidene compound crystallises in dark-red needles and melts at 142°, the 4-anisylidene derivative in orange-red crystals melting at 147°, and the 4-salicylidene compound in deep red needles melting at 196°.

5-Chloro-1-*p*-bromophenyl-3-methylpyrazole, $\begin{array}{c} \text{CH}:\text{CCl} \\ \text{CMe}:\text{N} \end{array} > \text{N} \cdot \text{C}_6\text{H}_4\text{Br}$,

crystallises in long, colourless needles, melts at 82°, and distils at 165° under 11 mm. pressure; it dissolves in concentrated hydrochloric acid, yields a sparingly soluble but somewhat unstable *platinichloride*, $(\text{C}_{10}\text{H}_8\text{N}_2\text{ClBr})_2 \cdot \text{H}_2\text{PtCl}_6$, a *methiodide* decomposing and melting at 254°, and yielding a *picrate*, $\text{C}_{11}\text{H}_{11}\text{N}_2\text{ClBr} \cdot \text{C}_6\text{H}_3\text{O}_7\text{N}_3$, melting at 170°, a *methobromide* melting at 260°, and a *methochloride* melting at 228°.

Monobromoantipyrine, $\begin{array}{c} \text{CH}=\text{C} \\ | \quad \text{O} < \\ \text{CMe}=\text{NMe} \end{array} > \text{N} \cdot \text{C}_6\text{H}_4\text{Br}$, obtained by treating

the methiodide, bromide, or chloride with alcoholic potash, crystallises from toluene or water in well-developed monoclinic prisms melting at 122° and boiling at 300° under 9 mm. pressure; it is readily soluble in most solvents and even dilute solutions exhibit the usual antipyrine reactions. Its *hydrochloride*, $\text{C}_{11}\text{H}_{11}\text{ON}_2\text{Br} \cdot \text{HCl}$, melts and decomposes at 213°, its *platinichloride* at about 208—210°, and its *ferrocyanide*, $(\text{C}_{11}\text{H}_{11}\text{ON}_2\text{Br})_2 \cdot \text{H}_4\text{FeC}_6\text{N}_6$, forms a perfectly white precipitate which turns blue on exposure to the air.

5-Bromo-1-*p*-bromophenyl-3-methylpyrazole, obtained by the action of ethyl bromide on the chloro-derivative, crystallises in colourless needles melting at 87—88°, and yields a *methiodide* melting at 259°. 5-Chloro-4-bromo-1-bromophenyl-3-methylpyrazole, obtained when the chloro-derivative is treated with a solution of bromine in light petroleum, forms colourless needles melting at 143°. 4:5-Dibromo-1-bromophenyl-3-methylpyrazole melts at 150—151°, and the corresponding 4:5-dichloro-compound at 134.5°; the latter yields a *methiodide* melting and decomposing at 236°.

5-Chloro-1-bromonitrophenyl-3-methylpyrazole is formed when the chloropyrazole is treated with the theoretical amount of concentrated nitric acid in the presence of sulphuric acid; it crystallises in colourless needles, melts at 115°, and on reduction yields the *amino*-compound which melts at 99—100°. A *dinitro*-compound melting at 158° is formed when fuming nitric acid is employed.

1-Bromophenyl-3-methylpyrazole forms colourless crystals melting at 94°, and yielding a *methiodide* which melts at 224°; with bromine, it yields 4-bromo-1-bromophenyl-3-methylpyrazole melting at 98°.

J. J. S.

5-Chloro-1-p-tolyl-3-methylpyrazole and Antipyrine-Bz*-carboxylic Acid. By AUGUST MICHAELIS and TH. SUDENDORF (*Ber.*, 1900, 33, 2615—2622. Compare preceding abstracts).—5-Chloro-1-p-tolyl-3-methylpyrazole, $C_{11}H_{11}N_2Cl$, forms colourless crystals, melts at 30° , distils at 148° under 12 mm., or at 274° under atmospheric pressure, dissolves in 20 per cent. hydrochloric acid and yields a *platinichloride*, $(C_{11}H_{11}N_2Cl)_2 \cdot H_2PtCl_6 \cdot 2H_2O$, which crystallises in orange-coloured needles. The *methiodide*, $C_{11}H_{11}N_2Cl \cdot MeI$, crystallises in needles melting at 245° and yields a *picrate* melting at 153° . With ethyl iodide, the product is 5-iodo-1-p-tolyl-3-methylpyrazole *ethiodide*, $C_{11}H_{11}N_2I \cdot EtI$, melting at 231° . The *methobromide* melts at 234° , and the *methochloride*, $C_{11}H_{11}N_2Cl \cdot MeCl \cdot H_2O$, when dehydrated, melts at 232° . When these compounds are treated with alcoholic potash or moist silver oxide they yield *p*-tolylpyrine.

5-Chloro-4-bromo-1-p-tolyl-3-methylpyrazole crystallises in long needles, melts at 66° , and has a characteristic ethereal odour; the 4:5-dichloro-compound melts at 57° .

5-Chloro-1-nitrotolyl-3-methylpyrazole crystallises in colourless, glistening needles, melts at 81° , and yields a *bromo-derivative* melting at 136° , identical with the compound obtained by nitrating 5-chloro-4-bromo-*p*-tolylmethylpyrazole. 5-Chloro-1-dinitro-*p*-tolyl-3-methylpyrazole melts at 167° . 1-*p*-Tolyl-3-methylpyrazole, obtained by reducing the chloropyrazole with hydriodic acid and red phosphorus, melts at 50° .

The most suitable oxidising agent for chlorotolylmethylpyrazoles is a sulphuric acid solution of chromium trioxide employed at temperatures below 30° . 5-Chloro-3-methylpyrazole-1-*p*-benzoic acid (5-chloro-

1-phenyl-3-methylpyrazole-Bz-*p*-carboxylic acid) $\left\{ \begin{array}{l} CH:CCl \\ CMe:N \end{array} \right\} > N \cdot C_6H_4 \cdot CO_2H$,

crystallises in felted needles melting at 206 — 208° and is insoluble in water or ether, but soluble in hydrochloric acid; when heated with baryta, it yields chlorophenylmethylpyrazole, and thus its constitution is established. The *barium* salt (with $3H_2O$) crystallises in needles, the *ethyl* ester is an oily liquid distilling at 271° , the *acid chloride* crystallises in needles melting at 82° and is readily decomposed by water, and the *anilide* crystallises in silky needles melting at 163° . When brominated, the acid yields 5-chloro-4-bromo-3-methylpyrazole-1-*p*-benzoic acid which crystallises in colourless needles melting and decomposing at 246° ; the same product is also formed when chlorobromotolylmethylpyrazole is oxidised with an aqueous acetic acid solution of chromic acid.

The *methiodide*, $C_{11}H_9O_2N_2Cl \cdot MeI$, melts at 264° , and on treatment with alcoholic potash or moist silver oxide yields *antipyrine-1-p-benzoic*

acid (*antipyrine-Bz-p*-carboxylic acid, $\left\{ \begin{array}{l} CH=C \\ O < \\ CMe=NMe \end{array} \right\} > N \cdot C_6H_4 \cdot CO_2H$, to-

gether with chloromethylpyrazolebenzoic acid methochloride. The former crystallises from hot water in glistening plates melting at 246° , and gives a faint red coloration with ferric chloride. J. J. S.

* The authors use this symbol to indicate that the carboxylic group is attached to a carbon atom of the benzene ring.

Aminomethylnaphthimidazolesulphonic Acid. By ALFRED GALLINEK (*Ber.*, 1900, **33**, 2315—2317).—5-Amino-2-methyl- α -naphthimidazole, described by Meldola and Streatfeild (*Trans.*, 1887, **51**, 691) as unstable, can be prepared from dinitroacetophthalide, and when treated with fuming sulphuric acid yields a *monosulphonic acid*, which crystallises with H_2O in microscopic, lustrous, four-sided plates, forms characteristic *calcium*, *sodium*, and *barium* salts, and a *diazo-compound*, which when boiled with dilute sulphuric acid yields a *hydroxysulphonic acid*. The base, sulphonic acid, and hydroxysulphonic acid, when coupled with tetrazo-compounds, give dyes of black, deep-blue and blue tints respectively, and not red, as would be expected from derivatives of aminonaphthalene. R. H. P.

Electrolytic Preparation of Benzidine. By WALTHER LÖB (*Ber.*, 1900, **33**, 2329—2333. Compare *Abstr.*, 1898, i, 14).—A good yield (80 per cent.) of benzidine is obtained by the electrolysis of a solution of azobenzene in concentrated sulphuric acid at 20—30° with a current of cathode density 3—5 amperes per 1 sq. dcm. with about 2·5—3 ampere-hours, a mercury cathode being used. Benzidine may be obtained (with a yield of 57—59 per cent. of the theoretical) directly by the electrolysis of nitrobenzene as follows: A 10 per cent. alcoholic solution of nitrobenzene containing 2 per cent. of sodium hydroxide is electrolysed in an earthenware cell with a current density of 3—5 amperes with 9 ampere-hours, a solution of sodium sulphate being used for the anode liquid; so soon as the whole is converted into azobenzene, the cathode liquid is strongly acidified with sulphuric acid dissolved in alcohol and again electrolysed, benzidine sulphate being precipitated as soon as it is formed. Nitrobenzene suspended in a weak alkaline solution can be similarly reduced to azoxybenzene, which, when electrolysed in acid solution, is reduced to benzidine. R. H. P.

3-Phenylpurine. By EMIL FISCHER and WOLF VON LOEBEN (*Ber.*, 1900, **33**, 2278—2281).—2:5:7-*Trichloro-3-phenylpurine*,
$$\begin{array}{c} \text{N}:\text{CCl}\cdot\text{C}=\text{N} \\ \text{CCl}\cdot\text{N}\cdot\text{C}\cdot\text{NPh} \end{array} \gg \text{CCl}$$
, obtained by heating dichloro-oxyphenylpurine with a mixture of phosphorus oxychloride and pentachloride in a sealed tube at 140° for 18 hours, melts at 210°—211°, and dissolves readily in hot acetic acid or chloroform, less easily in ether, and only very slightly in water; when quite pure it is colourless. It is easily soluble in concentrated sulphuric acid, and if the solution is heated for 15 minutes on the water-bath, hydrogen chloride is evolved, and dichloro-oxyphenylpurine produced.

When a solution of trichlorophenylpurine in alcohol (50 per cent.) is heated with zinc dust, *chloro-3-phenylpurine* separates in crystals; it melts at 162—163°, and dissolves easily in alcohol, less readily in ether or benzene, and is only slightly soluble in hot water. *Iodo-3-phenylpurine*, formed by the action of hydriodic acid on chlorophenylpurine, crystallises from hot alcohol in long, colourless needles, melts at 165—166°, and decomposes at a higher temperature with liberation of iodine; it is very slightly soluble in cold alcohol or hot water.

When iodophenylpurine is boiled with zinc-dust and water, *3-phenylpurine* is produced; it is obtained by sublimation under 5 mm. pressure

in colourless prismatic needles; it melts at 162—163°, is slightly soluble in boiling water, crystallises out in long needles, and is easily soluble in alcohol. The *hydrochloride*, *nitrate*, *platinichloride*, and *aureichloride* are described. E. G.

Triazan Derivative from Nitrosoformylphenylhydrazine. By ALFRED WOHL (*Ber.*, 1900, 33, 2759—2760).—*Nitrosoformylphenylhydrazine*, $\text{NO}\cdot\text{NPh}\cdot\text{NH}\cdot\text{CHO}$, obtained by the action of nitrous acid on formylphenylhydrazine, is an almost colourless substance which melts and decomposes at 84—85°, and dissolves readily in the ordinary organic solvents except light petroleum; it has acid properties and is soluble in dilute aqueous alkalis, from which it is precipitated by acids.

Formylphenylbenzylidenetriazan, $\text{CHPh}\cdot\text{N}\cdot\text{NPh}\cdot\text{NH}\cdot\text{CHO}$, prepared by reducing nitrosoformylphenylhydrazine in alcoholic solution with sodium amalgam and subsequent treatment with benzaldehyde, separates from benzene in crystals melting and decomposing at 182—183°; it has an acid character, being dissolved by dilute alkalis from which acids reprecipitate it unchanged. T. H. P.

Benzylhydrazine. By ALFRED WOHL and CARL OESTERLIN (*Ber.*, 1900, 33, 2736—2741).—*Benzylbenzylidenehydrazine*, $\text{CH}_2\text{Ph}\cdot\text{NH}\cdot\text{N}\cdot\text{CHPh}$, prepared by the partial reduction of benzalazine in alcoholic solution by means of sodium amalgam (2 atoms of sodium to 1 mol. of the azine), separates from its benzene solution on the addition of light petroleum in the form of white leaflets melting at 69—70° with evolution of nitrogen; it decomposes when kept with formation of benzaldehyde and on distillation gives rise to stilbene. *Acetylbenzylbenzylidenehydrazine*, $\text{CH}_2\text{Ph}\cdot\text{NAc}\cdot\text{N}\cdot\text{CHPh}$, forms colourless, stable leaflets melting at 79°.

Benzylhydrazine hydrochloride, obtained together with benzaldehyde on heating benzylbenzylidenehydrazine with dilute hydrochloric acid, crystallises from alcohol in long, white, four-sided plates which melt at 110°. *Benzylhydrazine*, $\text{CH}_2\text{Ph}\cdot\text{NH}\cdot\text{NH}_2$, formed from the hydrochloride on distillation with lime, is a colourless, viscous liquid which is miscible with water, alcohol, or ether and boils at 103° under 41 mm. pressure; it undergoes gradual decomposition and on distillation under the ordinary pressure nitrogen is evolved and dibenzyl formed. On oxidation in acid solution by means of ferric chloride, it yields benzalazine and hydrazine, whilst the action of iodine in sodium carbonate solution gives benzyl iodide and nitrogen. *Nitrosobenzylhydrazine*, $\text{C}_7\text{H}_7\cdot\text{N}_2\text{H}_2\cdot\text{NO}$, is very stable and on crystallising from boiling water melts at 71°; its vapours have no unpleasant smell or poisonous action. By the action of dilute mineral acids, the nitroso-compound is converted into *benzylazoimide*, $\text{C}_7\text{H}_7\cdot\text{N}_3$, a mobile oil which boils at 108° under 23 mm. pressure and explodes when strongly heated. T. H. P.

Action of Nitrous Acid on Benzylhydrazine. By THEODOR CURTIUS (*Ber.*, 1900, 33, 2561—2562).—*Nitrosobenzylhydrazine*, $\text{CH}_2\text{Ph}\cdot\text{N}(\text{NO})\cdot\text{NH}_2$, obtained by the action of nitrous acid on benzylhydrazine hydrochloride, forms colourless leaflets or needles and melts at 70°; it crystallises unchanged from water, shows the Lieber-

mann reaction, and has strongly reducing properties. When mixed in aqueous solution with benzaldehyde, no action occurs, but on adding dilute sulphuric acid, nitrosobenzylbenzylidenehydrazone, $\text{CH}_2\text{Ph}\cdot\text{N}(\text{NO})\cdot\text{N}:\text{CHPh}$, is formed.

Benzylazoimide, $\text{CH}_2\text{Ph}\cdot\text{N}_3$, obtained by warming nitrosobenzylhydrazine with dilute sulphuric acid, is a strongly refracting liquid which boils at 85° under 20 mm. pressure, is miscible with alcohol or ether, and has an odour recalling that of benzyl chloride; it is very stable towards hydrolytic agents.

Nitroso-p-methylbenzylhydrazine, $\text{C}_6\text{H}_4\text{Me}\cdot\text{CH}_2\cdot\text{N}(\text{NO})\cdot\text{NH}_2$, melts at 78° . W. A. D.

as-Dibenzylhydrazines. By MAX BUSCH and BRUNO WEISS (*Ber.* 1900, 33, 2701—2711. Compare *Abstr.* 1893, i, 410; 1898, i, 231).—*as-Dibenzylhydrazine* is best obtained by heating together hydrazine hydrate and benzyl chloride in dilute alcoholic solution.

Dibenzylbenzylidenehydrazine, formed as a bye-product in the preceding reaction, crystallises from alcohol in colourless needles or prisms and from petroleum in hexagonal plates; it melts at 87° . This substance is also obtained, together with benzylamine, by reducing dibenzylnitrosoamine with zinc dust and acetic acid.

as-o-Dinitrodibenzylhydrazine, $\text{NH}_2\cdot\text{N}(\text{CH}_2\cdot\text{C}_6\text{H}_4\cdot\text{NO}_2)_2$, prepared by mixing together cold alcoholic solutions of hydrazine hydrate and *o*-nitrobenzyl chloride, crystallises from alcohol in yellow needles and melts at 94 — 95° . Its *platinichloride* crystallises in yellow needles and melts at 142° .

o-Trinitrotribenzylhydrazine, $\text{N}_2\text{H}(\text{CH}_2\cdot\text{C}_6\text{H}_4\cdot\text{NO}_2)_3$, obtained as a bye-product in the preceding reaction, separates from a mixture of alcohol and chloroform in orange, prismatic crystals and melts at 180 — 181° .

o-Dinitrodibenzylnitrosoamine melts at 127° and not at 120° as indicated by Gabriel and Jansen.

Di-o-nitrodibenzylbenzylidenehydrazine, $\text{CHPh}\cdot\text{N}\cdot\text{N}(\text{CH}_2\cdot\text{C}_6\text{H}_4\cdot\text{NO}_2)_2$, produced by heating its generators on the water-bath, crystallises from alcohol in prisms and melts at 115 — 116° .

Formyldi-o-nitrodibenzylhydrazine, $(\text{CHO}\cdot\text{NH}\cdot\text{N}(\text{CH}_2\cdot\text{C}_6\text{H}_4\cdot\text{NO}_2)_2$, prepared by heating di-*o*-nitrodibenzylhydrazine with formic acid, crystallises from dilute alcohol in colourless needles and melts at 156° . The *diacetyl* derivative, obtained in a similar manner by the use of acetic anhydride, forms yellow prisms and melts at 125 — 126° .

Acetyldi-o-aminodibenzylhydrazine, $\text{NHAc}\cdot\text{N}(\text{CH}_2\cdot\text{C}_6\text{H}_4\cdot\text{NH}_2)_2$, is produced when di-*o*-nitrodibenzylhydrazine or di-*o*-nitrodibenzylnitrosoamine is reduced with zinc dust and acetic acid, it crystallises from benzene in colourless leaflets and melts at 153 — 154° . It is distinctly basic, dissolving readily in dilute mineral acids; the hydrochloride and platinichloride could not, however, be obtained crystalline. A *triacetyl* derivative results from the action of acetic anhydride on the preceding compound; this substance crystallises from alcohol and petroleum in colourless leaflets, melts at 239° , and is devoid of basic properties.

as-Di-p-nitrodibenzylhydrazine, $\text{NH}_2\cdot\text{N}(\text{CH}_2\cdot\text{C}_6\text{H}_4\cdot\text{NO}_2)_2$, prepared in

a similar manner to its ortho-isomeride, crystallises from alcohol in aggregates of needles melting at 137—180°; the *hydrochloride* crystallises in needles and melts at 242°.

Di-p-nitrodibenzylbenzylidenehydrazine forms yellow prisms and melts at 170°.

When *as*-dibenzylhydrazine is oxidised in alcoholic solution with mercuric oxide, the whole of its nitrogen is quantitatively liberated and dibenzyl is produced. *as*-Di-*o*-nitrodibenzylhydrazine and its para-isomeride undergo a similar change, and the corresponding dinitrodibenzyls are obtained.

Di-o-nitrodibenzylsemicarbazide, $\text{NH}_2 \cdot \text{CO} \cdot \text{NH} \cdot \text{N}(\text{CH}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{NO}_2)_2$, produced by heating an alcoholic solution of *o*-nitrobenzyl chloride and semicarbazide for 12 hours at 100°, is insoluble in the ordinary solvents and separates from glacial acetic acid in colourless prisms melting at 234°. G. T. M.

Reduction of Benzylidenehydrazine to Benzylhydrazine. By THEODOR CURTIUS (*Ber.*, 1900, 33, 2459—2460).—This reduction, which is otherwise difficult to accomplish, may be effected by shaking a solution of benzylidenehydrazine in absolute alcohol with 4 per cent. sodium amalgam at the ordinary temperature. The solution is then mixed with water and dilute hydrochloric acid, filtered from benzaldazine, and evaporated to dryness; the benzylhydrazine hydrochloride is extracted with hot absolute alcohol from the residue, which in addition contains the hydrochlorides of benzylamine and hydrazine.

C. F. B.

Nitrobenzylidenehydrazines. By THEODOR CURTIUS and A. LUBLIN (*Ber.*, 1900, 33, 2460—2466).—The nitrobenzylidenehydrazines, $\text{NO}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{CH} : \text{N} \cdot \text{NH}_2$, unlike benzylidenehydrazine itself, are comparatively stable substances, although they undergo transformation in moist air, probably into the tetrazones first and the aldazines finally. They are prepared by gradually adding alcoholic solutions of the nitrobenzaldehydes to a considerable excess of hydrazine hydrate. When oxidised in benzene solution with mercuric oxide, they form tetrazones, $\text{N}_2(\text{N} : \text{CH} \cdot \text{C}_6\text{H}_4 \cdot \text{NO}_2)_2$, which readily lose nitrogen forming aldazines, $\text{N}_2(\text{CH} \cdot \text{C}_6\text{H}_4 \cdot \text{NO}_2)_2$. When treated in alcoholic solution with acids they yield aldazines and hydrazine salts. They condense with aldehydes, $\text{R} \cdot \text{CHO}$, and ketones, CR_2O , to form mixed aldazines, $\text{NO}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{CH} : \text{N} : \text{N} : \text{CHR}$, and aldoketazines, $\text{NO}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{CH} : \text{N} : \text{N} : \text{CR}_2$, respectively. The compounds prepared are enumerated below with their melting points.

Nitrobenzylidenehydrazines: *m*-, yellow, 107°; *o*-, yellow, 76°; *p*-, orange-yellow, 134°, more stable than the others. *Dinitrobenzylidenetetrazones*: all reddish-brown and gummy. *Nitrobenzaldazines*: *m*-, yellowish, 194°; *o*-, 182° (apparently not new); *p*-, yellowish, 296°. *Nitrobenzalacetaldazines*: *m*-, grey, 68°; *o*-, red, decomposes before melting; *p*-, yellowish-grey, 140°, with decomposition. *Nitrobenzalbenzaldazines*: *m*-, yellow, 125°; *o*-, yellow, 105°; *p*-, yellow, 256°. *m*-*Nitrobenzal-o*-hydroxybenzaldazine: *m*-, yellow, 162°. *p*-*Nitrobenzalcinnamaldazine*, yellow, 169°. *Nitrobenzalacetoneazine*: *m*-, colourless, 91°; *o*-, yellowish-white, 70°; *p*-, yellow, 88°. C. F. B.

Preparation of Aromatic Aldehydes from the Corresponding Acids by Means of Hydrazine. By THEODOR CURTIUS (*Ber.*, 1900, 33, 2559—2561).—The product obtained by Davidis (*Abstr.*, 1897, i, 5) on heating dextrose with benzoylhydrazine and dilute aqueous sodium hydroxide, and thought to be a dextrose benzosazone, has been shown by Pinkus (*Abstr.*, 1898, i, 224) to consist of a mixture of the benzosazones of glyoxal and methylglyoxal; at the ordinary temperature, however, the dextrose does not enter into action, *benzoylbenzylidenehydrazine*, $C_6H_5 \cdot CH:N \cdot NH\text{Bz}$, being formed, owing to partial hydrolysis of the benzoylhydrazine occurring, accompanied by reduction of the benzoic acid to benzaldehyde by the hydrazine thus liberated. The product is sparingly soluble in all solvents, melts at $204\text{--}205^\circ$, and is easily hydrolysed by boiling dilute sulphuric acid to benzoic acid, benzaldehyde, and hydrazine.

[With H. MELSBACH.]—The conditions necessary to transform a large number of aromatic hydrazides into the corresponding tertiary hydrazones, $R \cdot CO \cdot NH \cdot N \cdot CHR$, have been investigated; on distilling these with dilute sulphuric acid, the corresponding aldehydes are easily isolated. In addition, it is shown that the ultimate product of the action of aqueous alkalis on aromatic hydrazines are aldazines of the type $CHPh \cdot N \cdot N \cdot CHPh$. W. A. D.

Tinctorial Properties of Diphenylcarbazone. By PAUL CAZENEUVE and PAUL SISLEY (*Bull. Soc. Chim.*, 1900, [iii], 23, 769—771).—Diphenylcarbazone, $NHPh \cdot NH \cdot CO \cdot N \cdot NPh$, resembles other colouring matters in its asymmetric character, but differs from them in containing the special auxochrome group, $CO \cdot NH$, which exhibits acid properties. Hence it dyes silk and wool directly, but the tint produced is fugitive and destroyed by dilute mineral acids. When metallic salts are used as mordants, more or less unstable tints ranging from rose to violet are produced, the brightest and most resistant being obtained with mercuric nitrate. N. L.

Influence of the Orientation of Chromophores on the Colour and other Properties of Dyes. By FRÉDÉRIC REVERDIN and PIERRE CRÉPIEUX (*Ber.*, 1900, 33, 2497—2503).—The azo-dyes derived from the nitro- and chloro-toluidines and 1-naphthol-4-sulphonic acid have been studied with a view of establishing a relationship between the colour of the compound and the orientation of its chromophores.

The bases obtained by nitrating aceto-*o*-toluidide and hydrolysing the crude product of nitration are most conveniently separated by distilling the solution of their hydrochlorides in steam, 3-nitro-2-toluidine passing over into the distillate whilst 5-nitro-2-toluidine remains in the residue.

In preparing 5-chloro-2-acetotoluidide, it is better to employ sodium chlorate and hydrochloric acid rather than free chlorine.

The azo-derivatives of the nitrotoluidines containing their nitro-radicles in the ortho- or meta-position relatively to the azo-group give practically the same shade of orange when dyed on wool from a dilute sulphuric acid bath. The colouring matter from 3-nitro-2-toluidine which contains a nitro-group in the para-position to the other chromophore is distinctly redder in colour. These compounds differ from one

another in their stability to light; the presence of a nitro-group in the ortho-position relatively to the azo-chromophore render the dyes more fugitive, that derived from the consecutive base 3-nitro-2-toluidine being the most sensitive of all.

The azo-compounds of 4:2- and 5:2-chlorotoluidines give redder shades than the corresponding derivatives of the chlorinated *m*- and *p*-toluidines but the consecutive base 6-chloro-2-toluidine yields the deepest yellow colouring matter.

Those azo-derivatives of the chlorotoluidines containing chlorine atoms in the ortho-position to the azo-groups are more fugitive than their meta- and para-isomerides; the consecutive arrangement of the three substituent radicles also diminishes the stability towards light.

There is no simple relationship between the solubility of these colouring matters and their constitution. G. T. M.

Action of Hypochlorous Acid on Primary Aromatic Amines. By WILHELM MEIGEN and W. NORMANN (*Ber.*, 1900, 33, 2711—2717).—Although the process described by Claus and Jaeck in the D. R.-P. No. 78748, is stated to be a general method for preparing azines by the action of hypochlorous acid on primary aromatic amines, yet this result is attained only in the case of β -naphthylamine and certain of its derivatives; α -naphthylamine and its sulphonic acids do not yield definite products; aniline and its homologues and their bromo-, nitro-, and sulpho-derivatives give rise to azo-compounds, and only from 2-nitro-*p*-toluidine is a small amount of a bye-product obtained, which is probably a nitrotolazine.

The aromatic base, dissolved in benzene, is shaken up with excess of the sodium hypochlorite solution, the product being obtained in a crystalline form on concentrating the solution of the hydrocarbon.

o-Dinitroazobenzene, obtained from *o*-nitroaniline, crystallises in straw-yellow, felted needles and melts at 194—195°. Corresponding azo-compounds are produced from the *m*- and *p*-nitroanilines; *m*-dinitroazobenzene agreeing in its properties with the substance described by Werner and Stiasny (this vol., i, 194).

2:2'-Dinitro-4:4'-azotoluene, prepared from 2-nitro-*p*-toluidine, crystallises in red leaflets and melts at 149°.

Sodium-1:2-naphthazine-6:6'-disulphonate, obtained by treating 2-naphthylamine-6-sulphonic acid with hypochlorous acid, forms a crystalline, greenish-yellow powder, which is soluble in water. Like $\alpha\beta$ -naphthazine, it develops a violet coloration with concentrated sulphuric acid. The sulphonic groups are not removed by heating with mineral acids, but the unsulphonated azine is produced in small quantities by the action of zinc dust. G. T. M.

Nomenclature of the Diazo-compounds. By ARTHUR HANTZSCH (*Ber.*, 1900, 33, 2556—2559).—Since no sharp line of demarcation can be drawn between diazo- and azo-compounds from consideration either of stability or colour, it is proposed that all compounds of the general type $R_1 \cdot N : N \cdot R_2$ be termed *azo*-compounds, irrespective of the nature of R_1 and R_2 ; the term diazo-compound is thus reserved only for fatty derivatives containing the group $C \begin{smallmatrix} N \\ | \\ N \end{smallmatrix}$. To the soluble, dissociating

forms of diazo-compounds, the term "diazonium" is still to be applied; but the derivatives hitherto spoken of as *syn*- and *anti*-diazo-compounds will now be named *syn*- and *anti*-azo-compounds. A list of revised names for typical substances is appended. W. A. D.

Decomposition of Diazonium Salts. By ARTHUR HANTZSCH (*Ber.*, 1900, 33, 2517—2541).—[With GUSTAV OSSWALD.]—The rate of decomposition of a number of diazonium salts by water was compared by measuring in each case the rate of evolution of nitrogen. The velocity constant of benzenediazonium chloride at 25° is 0.00068; of *p*-toluenediazonium chloride, 0.000081; of *p*-bromodiazonium chloride and anisole diazonium chloride, too small for measurement; and of *ψ*-cumenediazonium chloride, 0.0031. The introduction of halogens into the benzene nucleus thus diminishes the tendency of diazonium salts to undergo decomposition with water; moreover, tribromobenzenediazonium chloride is only decomposed on boiling with water, and then yields only resin and not tribromophenol. No relation exists, however, between the velocity constants of the formation of phenols and the affinity constants of the corresponding diazohydroxides; for although anisole and *ψ*-cumenediazonium hydroxides are equally strong bases, their rates of decomposition by water are entirely different.

[With W. SEMPLE.]—The decomposition of benzenediazonium chloride by 1 mol. of water yields 42 per cent. of phenol and 53 per cent. of chlorobenzene, whilst with 5 mols. of water only 46 per cent. of the latter is formed; with the corresponding diazonium bromide and 1 mol. of water, about 60 per cent. of bromobenzene is obtained. *ψ*-Cumenediazonium chloride, with 2 mols. of water, yields 52 per cent. of chloro-*ψ*-cumene, and the rest cumenol, whilst from the corresponding diazonium bromide 60 per cent. of bromo-*ψ*-cumene is obtained under similar conditions. With 1 mol. of glacial acetic acid, benzenediazonium chloride yields 57 per cent. of phenyl acetate and 43 per cent. of chlorobenzene, whilst with 10 mols., only 25 per cent. of chlorobenzene is produced; *ψ*-cumenediazonium bromide, with 2 mols. of acetic acid, yields 47 per cent. of cumenyl acetate and 53 per cent. of bromo-*ψ*-cumene, whilst with 40 mols., only 28 per cent. of the latter is obtained.

Benzenediazonium chloride, with cold absolute methyl alcohol, yields from 20 to 25 per cent. of anisole and a small amount of a hydrocarbon of high boiling point, probably diphenyl; on warming the same salt with ethyl alcohol, 25 per cent. of phenetole is obtained. With benzenediazonium bromide and methyl alcohol, the yield of anisole is only 10 per cent., but with ethyl alcohol, 30 per cent. of phenetole is obtained. *p*-Bromobenzenediazonium bromide yields, with ethyl alcohol, only a small quantity of *p*-bromoanisole, bromobenzene and resinous products being formed, whilst tribromobenzenediazonium bromide yields almost exclusively tribromobenzene and traces of tribromophenetole.

[With J. SPEAR.]—The decomposition of diazonium salts by hydriodic acid or potassium iodide in alcoholic or glacial acetic acid solution gives rise to large quantities of iodine, owing to the reduction by the hydriodic acid of the diazonium salt to the corresponding hydrocarbon.

In aqueous solution, the formation of iodine is diminished, but at the cost of production of phenol; increased dilution favours the liberation of iodine.

Benzenediazonium sulphate yields, with potassium iodide in *N*/20 solution at 10°, 40 per cent. of iodobenzene, the rest being transformed into phenol and resinous substances; *p*-toluenediazonium sulphate or chloride yields, in a similar solution at the ordinary temperature, 84 per cent. of *p*-iodotoluene, whilst *o*-toluenediazonium sulphate gave 53 per cent. of *o*-iodotoluene. *m*-Toluenediazonium sulphate, *as-m*-xylene-diazonium sulphate, and ψ -cumenediazonium sulphate, however, give rise only to the corresponding phenols without introduction of iodine into the nucleus, methyl groups thus impeding the latter action. Halogens, on the other hand, favour the introduction of iodine, for *p*-chlorobenzenediazonium sulphate, on boiling with *N*/20 aqueous potassium iodide, yields 72 per cent., *p*-bromobenzenediazonium sulphate 80 per cent., and tribromobenzenediazonium sulphate 94 per cent. of the iodo-derivative.

W. A. D.

Interaction of Diazonium Salts with Cuprous Compounds.

By ARTHUR HANTZSCH and J. W. BLAGDEN (*Ber.*, 1900, 33, 2544—2556).—Aqueous bromobenzenediazonium bromide interacts at 0° with cuprous chloride (1 mol.) suspended in water to form principally *p*-chlorobromobenzene, a small proportion only of *p*-dibromobenzene being obtained; *p*-bromobenzenediazonium chloride and cuprous bromide yield only *p*-dibromobenzene. When the copper haloid is dissolved in methyl sulphide and the diazonium salt added, either solid or dissolved in alcohol or glacial acetic acid, the action at 0° is similar, but more vigorous and complete. Cuprous iodide also yields, with diazonium chlorides or bromides, iodo-substituted benzenes; yet, mesitylene- and ψ -cumene-diazonium iodides with cuprous chloride yield as chief products the corresponding chloro- instead of the iodo-derivatives. The halogen introduced into the nucleus is thus derived principally from the cuprous salt, probably owing to the formation of an additive compound. In all these cases, a mixture of halogen derivatives is obtained.

syn-Diazocyanides are not changed by cuprous haloids even at the temperature of boiling methyl sulphide; yet, the *syn*-diazocyanides are rapidly converted into nitriles under the influence of copper powder, and diazonium haloids, by interaction with cuprous cyanide, form more nitrile than halogen-benzene. All attempts to prepare double salts of diazonium haloids with cuprous haloids failed, although double mercury salts of the type of *benzenediazonium nitrate mercuri-nitrite*, $2C_6H_5 \cdot N_2 \cdot NO_3 \cdot Hg(NO_2)_2$, are readily obtainable; the latter is precipitated on mixing concentrated solutions of potassium mercuri-nitrite and benzenediazonium nitrate, as an oil which rapidly crystallises. It is easily soluble in water, melts at 76°, and cannot be crystallised from water owing to its decomposing in the normal way to form phenol or nitrophenol; with copper powder, it yields nitrobenzene almost quantitatively. That the salt is not a double nitrite, $2C_6H_5 \cdot N_2 \cdot NO_2 \cdot Hg(NO_2)_2$, is shown by the fact that quite different substances are obtained on precipitating benzenediazonium sulphate

or chloride with potassium mercurinitrite, and that in these sulphuric acid and hydrochloric acid respectively are present. The double salts obtained with diazonium haloids are white, crystalline powders which are almost insoluble in water, and therefore do not decompose when stirred with copper powder; when boiled with water, they yield phenols.

On mixing solutions of potassium or sodium nitrite and cuprous chloride, a potassium cuprous nitrite is probably formed, since the mixture decomposes; for example, *p*-chlorobenzenediazonium sulphate forms *p*-nitrochlorobenzene along with *p*-dichlorobenzene. If, instead of the cuprous haloid, cuprous sulphite is employed, either in the form of the white Etard's salt, or, better, of the red cuprous cuprisulphite (Chevreul's salt), a nearly theoretical yield of nitro-derivative is obtained on decomposing the diazonium salt; this method of replacing the amino-group by a nitro-group is shown to give much better results than Sandmeyer's process in the case of *p*-chloroaniline, *p*-bromoaniline, tribromoaniline, and especially β -naphthylamine. That it is the nitrite radicle combined with the copper that replaces the diazonium group in these cases, as in the preceding, is shown by the fact that *p*-chlorobenzenediazonium chloride yields a mixture of 74 per cent. of *p*-chloronitrobenzene and only 26 per cent. of *p*-dichlorobenzene.

Attempts to introduce a nitroso-group in place of the diazonium radicle by means of "cuprous hyponitrite," and a fluorine atom by means of "cuprous fluoride," failed.

ψ -Cumenediazonium salts with cuprous haloids give rise to azo- ψ -cumene, the yield amounting to 50—70 per cent. of the theoretical.

W. A. D.

New Method of Preparing *iso*Diazotates. By EUGEN BAMBERGER and JENS MÜLLER (*Annalen*, 1900, 313, 97—128).—The authors have found that *o*- or *p*-hydroxybenzylated arylnitroso-derivatives of the type $\text{NO} \cdot \text{N} \cdot \text{Ar} \cdot \text{CH}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{OH}$, are resolved by very dilute potassium hydroxide into hydroxybenzyl alcohol and potassium isodiazotate, $\text{ArN} \cdot \text{N} \cdot \text{OK}$; the change does not occur when the hydroxy-group occupies the meta-position, or when other radicles replace hydroxyl.

Phenyl-o-hydroxybenzylnitrosoamine, $\text{OH} \cdot \text{C}_6\text{H}_4 \cdot \text{CH}_2 \cdot \text{NPh} \cdot \text{NO}$, crystallises from dilute methyl alcohol in pale yellow prisms melting at 131.5° . The hydrolysis was effected under very various conditions, which are fully described in the paper. Alkali was employed alone, or in presence of certain phenols, also at the temperatures of melting ice and boiling water; in each case, the isodiazotate was produced, and not the normal compound.

Phenyl-p-hydroxybenzylnitrosoamine crystallises from alcohol in flat, straw-yellow prisms and melts at 120° .

m-Hydroxybenzylideneaniline, $\text{OH} \cdot \text{C}_6\text{H}_4 \cdot \text{CH} \cdot \text{NPh}$, prepared from aniline and *m*-hydroxybenzaldehyde, crystallises from benzene in lustrous, colourless aggregates of prisms, and melts at 90.5 — 91° .

m-Hydroxybenzylaniline, $\text{OH} \cdot \text{C}_6\text{H}_4 \cdot \text{CH}_2 \cdot \text{NPh}$, obtained on reducing the Schiff base with sodium amalgam in alcohol, crystallises from dilute alcohol in short prisms and melts at 103 — 104° ; the *nitroso*-

derivative, $\text{OH} \cdot \text{C}_6\text{H}_4 \cdot \text{CH}_2 \cdot \text{NPh} \cdot \text{NO}$, separates from dilute alcohol in lustrous, colourless needles melting at $87.5-88^\circ$, and is practically indifferent towards alkali hydroxides.

o-Hydroxybenzyl-*p*-tolylnitrosoamine, $\text{OH} \cdot \text{C}_6\text{H}_4 \cdot \text{CH}_2 \cdot \text{N}(\text{C}_6\text{H}_4\text{Me}) \cdot \text{NO}$, crystallises from dilute acetic acid in feathery aggregates of colourless needles and melts at $74.5-75^\circ$; its behaviour towards alkali hydroxides resembles that of its lower homologue.

o-Chlorobenzylideneaniline, $\text{C}_6\text{H}_4\text{Cl} \cdot \text{CH} \cdot \text{NPh}$, prepared from aniline and *o*-chlorobenzaldehyde, is a yellow, viscous oil. *o*-Chlorobenzylaniline, $\text{C}_6\text{H}_4\text{Cl} \cdot \text{CH}_2 \cdot \text{NPh}$, obtained on reducing the Schiff base, is also a viscous oil, forming the crystalline *hydrochloride* which melts, not quite definitely, at $186-187^\circ$; the *nitroso*-derivative, $\text{C}_6\text{H}_4\text{Cl} \cdot \text{CH}_2 \cdot \text{NPh} \cdot \text{NO}$, separates from alcohol in pale yellow, lustrous leaflets melting at $53.5-54^\circ$, and is indifferent towards alkali hydroxides.

Other substances, which do not yield *isodiazotates* under the influence of alkali hydroxides, are *o*-nitrobenzylphenylnitrosoamine, which has been prepared by Busch, and *p*-nitrobenzylphenylnitrosoamine, $\text{NO}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{CH}_2 \cdot \text{NPh} \cdot \text{NO}$, which crystallises in pale yellow, transparent leaflets and melts at $75.5-76^\circ$.

Phenyl-as-o-hydroxybenzylhydrazine, $\text{OH} \cdot \text{C}_6\text{H}_4 \cdot \text{CH}_2 \cdot \text{NPh} \cdot \text{NH}_2$, prepared by reducing the nitrosoamine of *o*-hydroxybenzylaniline with zinc dust in acetic acid solution, is conveniently isolated in the form of the *m*-nitrobenzylidene derivative, $\text{C}_{20}\text{H}_{17}\text{O}_3\text{N}_3$, which crystallises from alcohol in radially disposed, orange red needles melting at $183-183.5^\circ$.

M. O. F.

syn-Diazotates from *p*-Bromodiazobenzene-*o*-sulphonic Acid. By DIMITER W. GERILOWSKI (*Ber.*, 1900, 33, 2317-2323).—*p*-Bromo-

benzenediazonium-*o*-sulphonic acid, $\text{C}_6\text{H}_3\text{Br} \begin{smallmatrix} \text{SO}_2 \\ \diagup \quad \diagdown \\ \text{N}(\text{:N}) \end{smallmatrix} \text{O}$, obtained by the diazotisation of *p*-bromoaniline-*o*-sulphonic acid, crystallises in silky, colourless, six-sided plates, decomposes at 149° , forms a neutral aqueous solution and does not detonate when struck. The

syn-disodium salt, $\text{SO}_3\text{Na} \cdot \text{C}_6\text{H}_3\text{Br} \begin{smallmatrix} \text{N} \\ | \\ \text{ONa} \end{smallmatrix}$, obtained by treating the acid

with sodium hydroxide below 0° , crystallises, with H_2O , in yellow crystals, forms an alkaline solution in water, couples instantly with β -naphthol and is quite stable when kept in a desiccator. The *anti-disodium* salt is obtained when the mother liquors left from the crystallisation of the *syn*-salt are heated; it crystallises in small clusters, and does not couple with an alkaline solution of β -naphthol until it has been converted into the isomeric form by acidifying and subsequent neutralisation. The corresponding *syn-dipotassium* salt crystallises, with $4\text{H}_2\text{O}$, in sharp-pointed plates, becomes reddish in colour when exposed to air, and, when heated to 100° , is converted into the *anti-dipotassium* salt, which crystallises, with H_2O , in dark, greenish-yellow, striated prisms.

R. H. P.

Diazohydrazides and Bisdiazotetrazones (Octazones). By ALFRED WOHL and HANS SCHIFF (*Ber.*, 1900, 33, 2741-2758).—By the action of diazobenzene sulphate on hippurylhydrazine, Curtius (*Abstr.*, 1893, i, 463) obtained a compound to which he gave the name

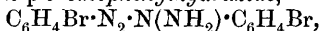
sym-hippurylphenylbuzylene, being derived from the hypothetical compound $\text{NH}\cdot\text{N}\cdot\text{NH}\cdot\text{NH}_2$. The authors have prepared a number of similar substances and suggest that it would be simpler to name them 'diazohydrazides,' which allows isomerides to be readily distinguished and is in better agreement with the chemical characters of the compounds. A study of the possible methods of condensation of a diazo-compound with a hydrazine with evolution of water, together with the fact that two isomeric compounds $\text{R}^{\text{I}}(\text{N}_4\text{H}_2)\text{R}^{\text{II}}$ and $\text{R}^{\text{II}}(\text{N}_4\text{H}_2)\text{R}^{\text{I}}$ exist which yield different oxidation products, shows that the diazohydrazides have the constitution $\text{NR}^{\text{I}}\cdot\text{N}\cdot\text{NR}^{\text{II}}\cdot\text{NH}_2$. Formation of these compounds takes place only at low temperatures and in presence of free acetic acid. They are mostly well crystallisable substances of a yellow or brown colour and more or less soluble in alcohol, ether, acetone, or benzene, less so in light petroleum, and, except in the case of derivatives of strongly basic hydrazines, insoluble in water or dilute acids. When heated on a spatula or with a hot glass rod, they explode but not when rubbed or struck. Those soluble in alkalis, such as diazobenzoic acid phenylhydrazide, reduce Fehling's solution. The yields obtained are small (in general 20—40 per cent.), as the reaction between the diazo-compound and the hydrazine goes partly in those directions which it takes in presence of mineral acids. On oxidation with permanganate, the diazohydrazides yield bisdiazotetrazones or octazones, which have the constitution $\text{NR}^{\text{I}}\cdot\text{N}\cdot\text{NR}^{\text{II}}\cdot\text{N}\cdot\text{N}\cdot\text{NR}^{\text{II}}\cdot\text{N}\cdot\text{NR}^{\text{I}}$ and contain the longest chain of nitrogen atoms known. They are generally light in colour but quickly darken under the action of light and air and explode when subjected to heat, friction, or impact; they dissolve in the organic solvents with the exception of light petroleum, but quickly decompose in solution.

Bisdiazobenzenediphenyltetrazone, $\text{N}_2(\text{NPh}\cdot\text{N}_2\text{Ph})_2$, obtained in small quantity on oxidising diazobenzenephénylhydrazide, melts at 51—52°.

p-Chlorodiazobenzenephénylhydrazide, $\text{C}_6\text{H}_4\text{Cl}\cdot\text{N}_2\cdot\text{NPh}\cdot\text{NH}_2$, melts at 78°; *p*-bromodiazobenzenephénylhydrazide, melts at 79°, and on oxidation with permanganate yields *bis-p*-bromodiazobenzenediphenyltetrazone, $\text{N}_2(\text{NPh}\cdot\text{N}_2\cdot\text{C}_6\text{H}_4\text{Br})_2$, melting at 60°.

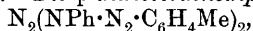
Diazobenzene-p-bromophénylhydrazide, $\text{NPh}\cdot\text{N}\cdot\text{N}(\text{NH}_2)\cdot\text{C}_6\text{H}_4\text{Br}$, melts at 69° and explodes 10° lower than its isomeride described above.

p-Bromodiazobenzene-*p*-bromophénylhydrazide,



melts at 82—84° and its oxidation product, *bis-p*-bromodiazobenzene-*di*-1:4-bromophényltetrazone, $\text{N}_2[\text{N}(\text{C}_6\text{H}_4\text{Br})\cdot\text{N}_2\cdot\text{C}_6\text{H}_4\text{Br}]_2$, at 58—61°.

p-Diazotoluenephénylhydrazide, $\text{C}_6\text{H}_4\text{Me}\cdot\text{N}_2\cdot\text{NPh}\cdot\text{NH}_2$, melts at 66—67°, and on boiling with dilute sulphuric acid, decomposes with brisk evolution of nitrogen and the formation of almost the theoretical quantity of *p*-cresol, together with phenylhydrazine sulphate, and a little diazotolueneimine. *Bis-p*-diazotoluenediphenyltetrazone,



melts at 64—67°, and dissolves slowly in ether with evolution of gas and formation of diazobenzenetoluidide.

Diazobenzene-p-tolylhydrazide, $\text{NPh}\cdot\text{N}\cdot\text{N}(\text{NH}_2)\cdot\text{C}_6\text{H}_4\text{Me}$, is a relatively stable compound melting at 64—65°, and on boiling with dilute

sulphuric acid yields phenol and *p*-tolylhydrazine sulphate. *Bisdiazobenzene-p-tolyltetrazone*, $N_2[N(C_6H_4Me) \cdot N_2Ph]_2$, melts at 55° .

m-Diazobenzoic acid phenylhydrazide, $CO_2H \cdot C_6H_4 \cdot N_2 \cdot NPh \cdot NH_2$, is an amorphous, yellow substance melting at $108-112^\circ$, and is soluble in aqueous sodium carbonate, giving a solution which reduces Fehling's solution; on boiling its benzene solution, it decomposes into the imine of diazobenzoic acid and aminobenzoic acid.

p-Diazobenzoic acid phenylhydrazide melts at $112-113^\circ$.

Diazobenzene-m-hydrazinobenzoic acid, $N_2Ph \cdot N(NH_2) \cdot C_6H_4 \cdot CO_2H$, melts at 86° , and on boiling with dilute sulphuric acid yields phenol and hydrazinobenzoic acid.

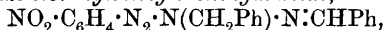
p-Nitrodiazobenzenemethylhydrazide, $NO_2 \cdot C_6H_4 \cdot N_2 \cdot NMe \cdot NH_2$, crystallises from benzene or aqueous alcohol in brown needles having a bronzy lustre and melting at $120-122^\circ$. By the action of benzaldehyde, it yields *p-nitrodiazobenzenebenzylidenemethylhydrazide*, $NO_2 \cdot C_6H_4 \cdot N_2 \cdot NMe \cdot N \cdot CHPh$; this separates from light petroleum in slender, yellowish-red needles which melt and evolve gas at 148° and explode at higher temperatures; it is readily soluble in acetone, less so in benzene, alcohol, ether, or acetic acid, and is precipitated unchanged from the last-named solvent by sodium carbonate.

Diazobenzenebenzylhydrazide, $N_2Ph \cdot N(NH_2) \cdot CH_2Ph$, crystallises from light petroleum in white, hexagonal leaflets which melt and evolve gas at $46-48^\circ$.

p-Nitrodiazobenzenebenzylhydrazide, $NO_2 \cdot C_6H_4 \cdot N_2 \cdot N(NH_2) \cdot CH_2Ph$, separates from alcohol in dark brown, shining, flat prisms melting at $94-96^\circ$, and exploding at a higher temperature; it dissolves readily in benzene or acetone, less so in alcohol or ether, and only slightly in acetic acid or light petroleum. Oxidation with permanganate does not yield the corresponding tetrazone derivative, but its decomposition products.

p-Nitrodiazobenzenebenzylamine, $NO_2 \cdot C_6H_4 \cdot N_2 \cdot NH \cdot CH_2Ph$, melts at 99° .

p-Nitrodiazobenzenebenzylbenzylidenehydrazide,



prepared either from *p*-nitrodiazobenzenebenzylhydrazide and benzaldehyde, or from nitrodiazobenzene and benzylbenzylidenehydrazone, crystallises from alcohol in pale yellow needles melting at $142-143^\circ$, and is soluble in benzene, acetone, light petroleum, ether, or acetic acid; it is a stable substance, and is only decomposed by long boiling with dilute acids.

T. H. P.

First Cleavage Product of Proteid by the Action of Alkali. By OTTO MAAS (*Zeit. physiol. Chem.*, 1900, 30, 61-74).—After the action of solution of the alkalis on egg-albumin and crystallised serum albumin, the following substances were sought for: (1) Proto- and hetero-albumose, by the addition of an equal volume of saturated ammonium sulphate; (2) A-albumose, by the addition of another volume of ammonium sulphate solution to the filtrate from (1); (3) B-albumose, by the saturation of the filtrate from (2) by ammonium sulphate; (4) C-albumose, by the addition of *N*/10 sulphuric acid to

the filtrate from (3); (5) peptone, by the occurrence of the biuret reaction in the final filtrate. A-, B-, and C-albumoses and peptone were absent, or present in the merest traces. The primary albumoses were not abundant, but the main product, called alkali-albumose, was precipitated by neutralisation; it resembles Gmelin's albuminic acid very closely. Its composition is, C, 53.57; H, 7.19; N, 13.62; S, 2.13; O, 23.49 per cent. Its rotatory power is $[\alpha]_D - 49.4$.

W. D. H.

Albumin in Ox-Serum. By HOUARDY (*Chem. Centr.*, 1900, ii, 682; from *Bull. Acad. roy. Belg.*, 1900, 401—413).—According to Halliburton the blood serum of hoofed animals contains two albumins coagulating at 77° and 82—84° respectively. The author's attempts to separate these albumins by fractional precipitation with ammonium sulphate have shown, however, that only one albumin is present although its temperature of coagulation is not constant. The following experiments on coagulation are also described. (1) Albumins which coagulated at 72° and 80° respectively, were found to be completely coagulated after heating for 5—6 hours at 65°. (2) The filtrate from a portion of the liquid, after heating for 3 or 4 hours at 65°, contained a small quantity of albumin which coagulated at 80—81°. (3) A neutral solution of albumin containing exactly 3 per cent. of ammonium sulphate was coagulated by heating to 72°. After filtering, the whole of the albumin was precipitated by ammonium sulphate and then dissolved in water so that the solution again contained 3 per cent. of ammonium sulphate. This solution was found to coagulate at 72° and on repeating the process, the third solution coagulated at 71° and the filtrate was free from albumin.

E. W. W.

Action of Dilute Acids, Alcohol, and Heat on Columbiniin. By ALEXEI A. PANORMOFF (*J. Russ. Phys. Chem. Soc.*, 1900, 32, 385—390. Compare *ibid.*, 1897, 29, 398; this vol., i, 126).—With hydrogen chloride, columbinin forms the compound $\text{Cb}, 5\text{HCl}$ and with hydrogen bromide, $\text{Cb}, 4\text{HBr}$, where Cb represents $\text{C}_{254}\text{H}_{415}\text{O}_{96}\text{N}_{56}\text{S}_2$. When the hydrochloride is heated with 0.1 per cent. hydrochloric acid, its specific rotation is increased but its composition remains unchanged. If precipitated from aqueous solutions by warming or by the addition of alcohol, columbinin is obtained in an insoluble form, whilst if the solution is evaporated in a vacuum, the columbinin obtained is soluble; the products obtained in this way are regarded as polymerides of columbinin.

T. H. P.

Colouring Matter of Blood. By MARCELLUS NENCKI AND J. ZALESKI (*Zeit. physiol. Chem.*, 1900, 30, 384—435. Compare *Abstr.*, 1885, 69, 70, 566, 825, 826; 1896, i, 516, 660; 1897, i, 207, 232; 1898, i, 542; 1899, ii, 440). I. *Hæmin Ethers*.—When hæmoglobin is extracted with an acetic acid solution of sodium chloride by the Teichmann-Schalféeff method (*Abstr.*, 1885, 69) the product is *acetyl-hæmin*, $\text{C}_{34}\text{H}_{33}\text{O}_4\text{N}_4\text{ClFe}$; the same product is obtained from the blood of the dog, horse, cow, cat, and goose. It crystallises in microscopic

triclinic plates and prisms, readily dissolves in dilute alkalis, ammonia, or solutions of organic bases, but is insoluble in dilute mineral or organic acids. It probably contains both chlorine and acetyl attached to the iron atom, as when the latter is removed by the action of hydrobromic acid, both chlorine and the acetyl group are withdrawn from the molecule. Cold sodium hydroxide removes chlorine and acetyl group but not iron; the hydrolysis is not complete as the hæmatin thus obtained always contains minute quantities of chlorine. The hæmin obtained by Nencki and Sieber's method yields the same hæmatin on hydrolysis. Acetyl hæmin contains no alkyl groups attached to oxygen or nitrogen, but two hydroxyl groups are present, as it readily yields mono- and di-ethers. The substances obtained by different authorities by the action of alcohols and hydrochloric acid on hæmoglobin are probably ethers of hæmin or of acetyl hæmin.

Hæmin dimethyl ether, $C_{32}H_{29}(OMe)_2ON_4ClFe$, obtained when acetyl hæmin is dissolved in a chloroform solution of quinine and then treated with methyl alcohol saturated with hydrogen chloride, forms whetstone shaped crystals, is completely insoluble in alkalis, and does not melt at 300° . *Acetyl hæmin ethyl ether* is identical with the compound described by Mörner as β -hæmin; when boiled with potassium hydroxide it evolves ethyl alcohol, and dissolves readily as it contains a free hydroxyl group. *Acetyl hæmin diethyl ether* forms black, cubical crystals and is insoluble in alkalis. Cloetta's hæmin hydrochloride is essentially a mixture of the di- and mono-ethyl ethers. The *amyl ether*, $C_{34}H_{32}(C_5H_{11})O_4N_4ClFe$, forms spindle-shaped crystals readily soluble in chloroform, but only sparingly so in aqueous ammonia, it does not melt at 350° . In the preparation of these ethers, the formation of large hexagonal plates has been observed, but their composition has not been determined.

When hæmoglobin is extracted with acetone, the product is not homogeneous, but contains dark coloured hair-like needles, which appear to be *hæmin*, $C_{32}H_{31}O_3N_4FeCl$, as on treatment with acetic acid they yield the acetyl hæmin already described. When ethyl acetate and hydrochloric acid are employed as extractive agents, the product consists of acetyl hæmin and its ethyl ether.

The authors do not consider Preyer's synthesis of hæmoglobin (Abstr., 1897, i, 304) as established.

II. *Hæmatoporphyrin*.—In the preparation of hæmatoporphyrin (Abstr., 1888, 971), it is advisable to use small quantities of hæmin, and to leave it in contact with concentrated hydrobromic acid for three days at the ordinary temperature. Hæmin, acetyl hæmin, and its ethers all yield the same hæmatoporphyrin, $C_{16}H_{18}O_3N_2$ (compare Bialobrzewski, Abstr., 1897, i, 208, and Küster, *ibid.*, 232). It yields an unstable *ammonium* salt and a *dimethyl ether*, $C_{16}H_{16}(OMe)_2ON_2$, which forms an amorphous, brick-red powder, and readily turns brown; it begins to sinter at 60° , and is completely melted at 85° . The *diethyl ether* also melts below 100° , evolving ethyl alcohol; it is insoluble in dilute acids or alkalis, and only sparingly soluble in ether or benzene. An *anhydro-monoacetyl hæmatoporphyrin*, $C_{32}H_{31}AcO_4N_4$, obtained by the action of acetic anhydride and sodium acetate, forms an amorphous, brown-red powder.

All attempts to remove the oxygen atoms from hæmatoporphyrin proved unsuccessful. J. J. S.

Crystals from Pigeons' Blood. By ARTHUR SCHWANTKE (*Zeit. physiol. Chem.*, 1900, 29, 486—491).—Sphenoidally-hemihedral tetragonal crystals [$a:c=1:1.175$] of oxyhæmoglobin obtained from pigeons' blood are described, with drawings of the different habits assumed; the crystals are characterised by a tendency to parallel growth, and can be kept several months at a low temperature without the brightness or relative distribution of the faces being impaired, although internally the crystals lose their transparency and become isotropic. W. A. D.

Hæmatin and Hæmochromogen obtained by the use of Pepsin-hydrochloric Acid. By RICHARD VON ZEYNEK (*Zeit. physiol. Chem.*, 1900, 30, 126—134).—Hæmatin obtained by different methods has been analysed, and different results obtained. The method recommended here is to digest a solution of hæmoglobin crystals with pepsin-hydrochloric acid. Tryptic digestion leads to no result. At the end of some days, the bulk of the hæmatin so formed is precipitated as a brown powder; this is suitably washed and collected, and from it hæmin crystals are prepared by the addition of acetone and hydrochloric acid. The crystals are dichroic, and belong either to the monoclinic or triclinic system. Analytical results correspond with those required for the formula $C_{34}H_{34}O_4N_5ClFe$, containing one atom of nitrogen more than in Hoppe-Seyler's and Mörner's preparations. If dissolved in dilute alkali, a precipitate of hæmatin of the formula $C_{34}H_{35}O_5N_5Fe$ is obtained on adding dilute sulphuric acid. From this, hæmochromogen can be prepared. It is doubtful from the analyses whether the formula for this substance is $C_{34}H_{38}O_4N_6Fe$ or $C_{68}H_{76}O_9N_{12}Fe_2$. By electrolysis of hæmatin solutions, hæmochromogen was not obtained. If pyridine is added to a solution of hæmatin and then hydrazine hydrate, hæmochromogen is produced. W. D. H.

Aldehydase from the Liver and Suprarenal Capsule. By MARTIN JACOBY (*Zeit. physiol. Chem.*, 1900, 30, 135—148. Compare Abstr., 1899, ii, 778).—The oxidising ferments in the liver are probably numerous; the one investigated in the present research is termed *aldehydase* and oxidises salicylaldehyde. A similar ferment can be separated from the cortex of the suprarenal capsule. Evidence is adduced that the action is fermentative. It was separated from aqueous extracts of the liver by precipitation with ammonium sulphate, the ferment coming down with the final fractions; the precipitate was dissolved in water, again precipitated with alcohol, and again dissolved in water; this solution was made faintly alkaline to prevent precipitation of proteids, and precipitated with uranium acetate; the final precipitate was dissolved in water. The enzyme is a colloid (non-dialysable); under a pressure of 6 atmospheres, however, it passes through a porcelain cell. It is not proteid, and does not give the biuret or Millon's reaction. W. D. H.

Proteolytic Enzyme of Germinated Barley. By WILHELM WINDISCH and B. SCHELLHORN (*Chem. Centr.*, 1900, ii, 489—490, 490—491; from *Woch. Bräw.*, 17, 334—336, 437—439, 449—452).—From their lengthy researches on the proteolytic enzyme contained in malt, the authors draw the following conclusions: (1) Under conditions favourable to the action of animal enzymes, the enzyme does not attack albumin which has been rendered insoluble; (2) the enzyme only gives the biuret reaction when it is in contact with albumins or albuminous substances of animal origin; (3) the decomposing action of the enzyme can only be recognised by its action on albumins which are in a soluble form.
E. W. W.

Galactase, the Proteolytic Ferment peculiar to Milk, its Properties, and Action on the Proteids of Milk. By S. MOULTON BABCOCK and H. L. RUSSELL (*Centr. Bakt. Par.*, 1900, [ii], 6, 17—21, 45—50, and 79—88).—Galactase (previously described by the authors, *Centr. Bakt. Par.*, [ii], 3, 615) is a proteolytic ferment similar to trypsin and is present in the milk of all animals. It is more active in moderately alkaline than in neutral or faintly acid solutions. Comparative experiments are described, in which the action of all proteolytic ferments of animal origin on milk is tabulated.

Pepsin differs from all other proteolytic ferments in that it causes no alteration in the amount of soluble nitrogen compounds in milk which has been treated with other ferments. A large proportion of the nitrogen present in milk is not attacked by these ferments, the greater part of this is the nuclein of the proteid molecules, but some is due to the accumulation of decomposition bye products, which hinder the digestion. The proteids are attacked by all the ferments with the formation of albumoses, amino-compounds, and sometimes even ammonia. Trypsin and pancreatin differ from galactase and from the proteolytic ferment derived from a culture of *Bacillus subtilis* in not forming ammonia; galactase differs from the latter in that the nitrogen compounds formed in digestion by its agency are more equally divided in albumoses, peptones, amides, and ammonia.
R. H. P.

The Organised Ferment present in Milk, the so called Galactase. By ED. VON FREUDENREICH (*Centr. Bakt. Par.*, 1900, [ii], 6, 332—338. Compare *ibid.*, 3, 615).—The author has repeated and confirms the researches of Babcock and Russell (*loc. cit.* and preceding abstract). Formalin or a temperature of 75° weakens the action of the galactase.
R. H. P.

JOURNAL

OF

THE CHEMICAL SOCIETY.

ABSTRACTS OF CHEMICAL PAPERS PUBLISHED IN
BRITISH AND FOREIGN JOURNALS.

PART II.

General and Physical Chemistry.

Influence of Slight Impurity on the Spectrum of a Gas. By PERCIVAL LEWIS (*Ann. Phys. Chem.*, 1899, [ii], **69**, 398—425).—The spectrum of pure hydrogen was compared with that obtained when the gas contained small quantities of (*a*) mercury vapour, (*b*) oxygen, (*c*) water vapour, external electrodes being employed. With the apparatus used, the intensity of the hydrogen spectrum was a maximum at a pressure of 3 mm. When a small trace of mercury vapour was present, the green mercury line appeared in the spectrum at all temperatures above -20° , its intensity being for a given hydrogen pressure proportional to the density of the mercury vapour. The appearance of the mercury line was accompanied by a diminished intensity of both the simple and compound hydrogen spectra. For pressures less than 6 mm., the relative intensities of the hydrogen and mercury spectra appear to be proportional to their densities; the addition of 4 per cent. of mercury vapour to pure hydrogen diminishes by half the intensity of the latter spectrum.

When hydrogen contains a small quantity of oxygen, the intensity of the hydrogen spectrum is increased if the pressure is less than 1.5 mm., and diminished if the pressure is greater. The similarity of the effect produced by water vapour is probably to be explained by the formation of the latter, when a discharge passes through hydrogen containing a trace of oxygen.

The observations made lead to the conclusion that the compound spectrum is really characteristic of hydrogen, and not due to any impurities.

The spectrum of oxygen containing a trace of mercury vapour gave no evidence of the presence of the latter; the addition, however, of a trace of hydrogen was followed immediately by the appearance of the green mercury line, a phenomenon which it is difficult to explain satisfactorily. J. C. P.

Phototropy. By WILHELM MARCKWALD (*Zeit. physikal. Chem.*, 1899, 30, 140—145).—The anhydrous chloride of quinoquinoline (Abstr., 1894, i, 474), on exposure to light, changes in colour from yellow to an intense green, and returns to its original state immediately at 90°, or in the dark at ordinary temperatures in a few days. The change is brought about in a few seconds by bright sunlight, and in a few minutes by diffused daylight, and is chiefly due to the more refrangible rays: Röntgen rays have no effect. Similar changes are obtained with β -tetrachloro- α -ketonaphthalene (Abstr., 1888, 710), which, by crystallisation from solvents, forms colourless, transparent crystals; these, when powdered and exposed to light, change to an amethyst colour, whilst large crystals become pleochroic, exhibiting a reddish-violet colour in one direction. The change does not appear to be connected with any chemical or crystallographic alteration, and by fusion a non-sensitive modification can be obtained which slowly returns to the sensitive form. To these phenomena, the author applies the term phototropy. L. M. J.

Concentration-cells with Unalterable Electrodes. By KARL SCHAUM (*Zeit. Elektrochem.*, 1899, 5, 316—319).—If two electrodes of a material which is not acted on by the electrolytes to be employed are immersed in solutions of an oxidising agent and of the substance formed by its reduction, a galvanic cell is formed, the E.M.F. of which is proportional to the absolute temperature, and depends on the relative concentrations of the ions present, but not on their chemical nature.

The E.M.F. is given by the formula $E = RT/ne \log.(c_1 c'_2)/(c_2 c'_1)$, where n is the difference between the number of electrical charges carried by the ion in question in its higher and lower stages of oxidation, $e = 96540$ coulombs, c_1 and c_2 are the concentrations of the ions of the higher and lower stage of oxidation respectively in one solution, and c'_1 and c'_2 the same quantities in the other solution.

Some experiments with solutions containing potassium ferro- and ferri-cyanides and platinum electrodes gave numbers which were in satisfactory agreement with the requirements of the formula.

T. E.

Theory of Lead Accumulators. By F. DOLEZALEK (*Zeit. Elektrochem.*, 1899, 5, 533—539).—In a previous paper (Abstr., 1898, ii, 551), the author obtained, by thermodynamics, a formula showing the relation between the E.M.F. of a lead accumulator and the concentration of the sulphuric acid used in it. For concentrations not exceeding 1 gram-molecule per litre, this may be simplified to the form,

$$E_2 - E_1 = 0.000198 \nu T [\log_{10} c_2/c_1 + 0.009 (c_2 - c_1)]$$

where E_1 and E_2 are the E.M.F.s of accumulators containing acid of

the concentrations c_1 and c_2 respectively, and ν is the average number of ions formed from 1 molecule of sulphuric acid. The same formula is obtained by means of Nernst's osmotic theory, whether the theory of the chemical action of the accumulator due to Liebenow or that due to Le Blanc is assumed to be true. The formula is shown to be in good agreement with experimental results.

The E.M.F. of an accumulator filled with a saturated solution of lead sulphate is 1.25 volts at 0° . Combining this with the E.M.F. found for an acid of known concentration, it is easy to calculate, from the formula, the concentration of the sulphuric acid formed by hydrolytic dissociation in the lead sulphate solution. The calculation shows that 15 per cent. of the lead sulphate has suffered hydrolytic dissociation.

The E.M.F. of an accumulator containing a saturated solution of lead oxide in $N/10$ sodium hydroxide solution is 0.8 volt, and this is shown to be practically identical with the E.M.F. which an accumulator filled with pure water would possess. From this, the concentration of the hydrogen ions in pure water is readily calculated to be 0.33×10^{-7} gram-mol. per litre, in excellent agreement with the determination of Kohlrausch and Heydweiller.

Measurements are made of the difference of potential between a hydrogen electrode and the positive or negative plate of an accumulator in sulphuric acid of various concentrations, which are also shown to be in agreement with the author's theory. Similar measurements and calculations are made with a mercury-mercurous sulphate electrode.

The results obtained with the hydrogen electrode are of interest in connection with the gradual discharge of accumulators when not in use. This is due to the presence of particles of impurities in the plates which give rise to local electrolytic action; on the lead plate, hydrogen must be evolved on the surface of the impurity giving rise to a hydrogen-lead couple, on the peroxide plate, oxygen is evolved on the surface of the impurity, producing a lead peroxide-oxygen couple. The E.M.F.'s of these couples in acids of different concentration are as follows:—

	4.86	9.33	19.76	26.36	52.93 per cent. H_2SO_4 .
$PbO_2:O_2$	0.55	0.56	0.59	0.62	0.72 volt.
$Pb:H_2$	0.27	0.28	0.32	0.34	0.43 volt.

Since the E.M.F. of the couples and the conductivity of the acid both increase as the concentration of the acid increases, the rate of discharge of the plates increases rapidly with increasing concentration of the acid, which is quite in accordance with practical experience. T. E.

Dielectrical Researches and Electrical Waves. By W. D. COOLIDGE (*Ann. Phys. Chem.*, 1899, [ii], 69, 125—166).—An electrical resonance method of determining the dielectric constant is described, which differs from that of Drude (compare Abstr., 1897, ii, 438) in that the condenser with the substance to be examined is in the oscillating system instead of in the receiving system. Comparison of the results obtained with a number of esters shows the method to be trustworthy and accurate; the author estimates that, by a few measurements,

the dielectric constant can be determined with a probable error of only 0.1 per cent.

At 14°, the dielectric constants of several liquefied gases have the following values: sulphur dioxide, 13.75; ammonia, 16.2; chlorine, 1.88. Linde found 14.8 for the sulphur dioxide constant at 23°, and 1.93 for the chlorine constant at 14°.

The temperature coefficient of the dielectric constant of water is found to be -0.432 per cent. at 17°, a value agreeing with the results of Drude and Heerwagen.

The anomalous absorption of water, previously observed up to $\lambda = 10$ cm., can, by the author's method, be determined up to $\lambda = 147$ cm., for which wave-length the absorption index $= 0.0082$. The absorption indices of a few esters have also been determined.

The value 4.35 is found for the dielectric constant of ether at 17.8°, in close agreement with Drude's determination. Experiments with mixtures of ether and chloroform confirm the existence of a maximum dielectric constant, found by Philip (compare Abstr., 1898, ii, 9) by a slow vibration method.

From the formula,

$$(\sqrt{e} - 1).100/d = (\sqrt{e_1} - 1).p_1/d_1 + (\sqrt{e_2} - 1)(100 - p_1)/d_2,$$

where e, e_1, e_2 are the dielectric constants of a mixture and its two components, d, d_1, d_2 the corresponding densities, and p_1 the percentage of one component; the author has calculated the dielectric constants of a number of alcohols in dilute benzene and toluene solution. These calculated dielectric constants diminish with falling concentration, and approach limiting values agreeing closely with those determined by Philip (*loc. cit.*) with Nernst's apparatus. Thus for the alcohols slow and rapid vibration methods lead to the same limiting values, which may be considered free from electrical dispersion.

The paper contains also a theoretical discussion of the method employed and the phenomena described. J. C. P.

Electrical Charges of freshly prepared Gases from Electrolytic Sources. By WILHELM KÖSTERS (*Ann. Phys. Chem.*, 1899, [ii], 69, 12—33).—The author confirms Townsend's results (*Phil. Mag.*, 1898, [vi], 45, 125), who showed that gases obtained by electrolysis have a positive or negative charge, according to the nature of the gas and the electrolyte employed, but rejects the theory that the phenomenon is to be explained by the escape of undischarged ions from the electrolyte. A connection is rather suggested with the observation of Lenard (*Ann. Phys. Chem.*, 1892, [ii], 46, 584), that air is negatively electrified when falling drops of water encounter an obstacle, and with the closely allied phenomenon of a gas being electrified by its passage through water.

Gases rendered non-electric and freed from dust particles by filtration through a tube connected to earth and filled with moist cotton wool were bubbled through various electrolytes. A comparison of the electrification produced with that obtained in electrolytic gases showed that the charges in the two cases generally agreed in sign, but were not at all proportional in quantity. Further, the ratio of the

charge to the volume of gas was much greater in the case of the electrolytic gases, but experiment showed that this might be due to the presence of fine particles of the electrolyte.

When hydrogen is bubbled through pure water, the former acquires a considerable negative charge; this action, however, is prevented by very small quantities of any dissolved substance. For a number of inorganic acids and salts, the electrifying action is found to vary with the concentration in a similar manner. In concentrated solutions, the action either is *nil* or approaches that value. The electrification of hydrogen bubbled through sulphuric acid of sp. gr. 1.3 is independent of the temperature. Absorption of the gas by the liquid slightly diminishes the electrification produced.

J. C. P.

Change of Resistance of Lead Dioxide. By TH. SUNDORPH (*Ann. Phys. Chem.*, 1899, [ii], 69, 319—323).—When two brass rods, separated by a layer of lead dioxide, have a potential difference of 33 volts (the exact value depending on the state of compression of the dioxide), the current produced first increases, and then decreases, reaching finally a constant value. This behaviour is probably due to the heat developed, which is greatest at the positive electrode, and to the formation of badly conducting monoxide. When the heat is supplied externally, and the current strength is determined at intervals, the latter is found to change in the same way as before. The period during which the current strength increases is lengthened when the potential is less than 33 volts, and shortened when the potential is greater than 33 volts, ultimately vanishing altogether. In the latter case, the rise of temperature is slight, and the amount of dioxide decomposed small compared with the great and sudden increase of resistance; the decomposition is probably due to sparks, chiefly in the neighbourhood of the electrodes.

J. C. P.

Electrolytic Conductivity of Pure Substances. By RICHARD ABEGG (*Zeit. Elektrochem.*, 1899, 5, 353—355).—In order that a pure substance shall possess electrolytic conductivity, its chemical constitution must be such that ions may be formed from it, its dielectric constant should be high, and it should not contain a large proportion of polymerised molecules, since these cannot dissociate directly into ions. Many substances with large dielectric constants (water, methyl and ethyl alcohols, formic acid) consist mainly of polymerised molecules and are therefore bad conductors. Others, with large dielectric constants and small polymerisation, are unsuitably constituted; nitrobenzene, ethyl nitrate, and benzonitrile, for example, contain the groups NO_2 , NO_3 , and CN , which readily form ions, but on the other hand, they contain the groups C_6H_5 and C_2H_5 , which have never been observed in the form of ions.

Fused salts, in all probability, possess high dielectric constants, their chemical constitution is very favourable to the formation of ions, nothing is known of their association factor. They form the only group of pure substances with any considerable electrolytic conductivity.

In the case of solutions, it is extremely probable that the capacity of the ions to unite with molecules of the solvent has an important

influence on the degree of dissociation. Solutions in water and liquid anhydrous ammonia are mentioned as illustrations of this.

T. E.

Influence of Substituents on the Electrical Conductivity of Benzoic Acid. By ALFRED TINGLE (*J. Amer. Chem. Soc.*, 1899, 21, 792—803).—The conductivities of the alkali salts of benzoic acid and several halogen derivatives have been determined in aqueous solution for $v=64$ and $v=128$. The numbers obtained do not agree with the rule that the difference between the conductivities of two metals is constant, and independent of the acid with which they are combined; the deviation from this rule is most marked in the case of sodium and potassium iodobenzoates.

J. C. P.

Electrical Conductivity of Non-aqueous Solutions. By AZARIAH T. LINCOLN (*J. Physical Chem.*, 1899, 3, 457—494).—The paper contains an account of an extensive investigation of the electrical conductivity of solutions of inorganic salts in solvents other than water. The compounds employed were the chlorides of aluminium, chromium, manganese, zinc, cobalt, nickel, copper, cadmium, arsenic, tin, potassium and lithium, nitrates of lead and silver, cyanides of mercury and silver, and copper sulphate, while as solvents the following liquids were used:—Ethyl, propyl, allyl, benzyl alcohols; benzaldehyde, salicylaldehyde, furfuraldehyde, acetone, methyl propyl ketone, acetophenone, ethyl acetate, ethyl monochloroacetate, ethyl cyanoacetate, ethyl acetoacetate, ethyl benzoate, ethyl oxalate, ethyl nitrate, amyl nitrite; nitrobenzene *o*-nitrotoluene, aniline, xylidine, benzonitrile, pyridine, piperidine, quinoline, phosphorus trichloride, and tin tetrachloride. Although with methyl and ethyl alcohols, limiting values for the molecular conductivity were reached, yet as a general rule this is not the case, and the values for the dissociation in propyl alcohol given by Schlamp (*Abstr.*, 1894, ii, 376) are, on this account, not justified. Solutions in ketones conduct, the highest values being obtained with acetone; in some cases, the molecular conductivity was found to decrease after certain dilutions. Pyridine yields conducting solutions, as does nitrobenzene, but here also limiting values are seldom indicated. It hence follows that as a general rule dissociation values cannot be calculated except in a few cases with alcoholic solutions, and in these the agreement of the values with those obtained by other methods is not satisfactory. Many conducting solutions have been found to give normal molecular weights by the boiling point methods, as, for example, solutions in acetone (Dutoit, *Abstr.*, 1899, ii, 350), and in benzonitrile and pyridine (Werner, *Abstr.*, 1897, ii, 214), so that in non-aqueous solutions there is no agreement between the evidence concerning dissociation afforded by the different methods. In alcoholic solutions also, in which considerable dissociation occurs, the results are not in accord with the dilution law of either Ostwald or Rudolphi. Examination of the degrees of association of the various solvents used indicates that the theories of Dutoit and of Crompton (*Trans.*, 1897, 71, 925), that only associated solvents yield conducting solutions, are untenable, inasmuch as many solutions of high conductivity were

obtained with non-associated solvents. Comparisons of dielectric constants show that while, as a general rule, solvents with high constants yield solutions that conduct well, yet there is no proportionality between the two values (see Brühl, *Abstr.*, 1899, ii, 735; this vol., ii, 11). The author hence considers that the dissociation theory, in its present form, cannot be applied to explain the conductivity of non-aqueous solutions, and urges the desirability of obtaining further data (compare *Abstr.*, 1899, ii, 397; also Kahlenberg, *Abstr.*, 1899, ii, 624).

L. M. J.

Electrolytic Gas Development. By WILLIAM A. CASPARI (*Zeit. physikal. Chem.*, 1899, 30, 89—97).—At ordinary temperatures, hydrogen is liberated at 1.55 to 1.56 volts, and with higher E.M.F.'s a mixture of oxygen with excess of hydrogen is obtained, whilst at a temperature of 98° to 100°, hydrogen production occurs at 1.33 volts (see Le Blanc, *Abstr.*, 1894, ii, 4; Nernst, *Abstr.*, 1897, ii, 394). After long electrolysis, hydrogen peroxide or persulphuric acid is present in the liquid. With electrodes of spongy platinum, the cathodic electrolysis is completely reversible; with bright platinum, a slight excess of tension was necessary for the liberation of hydrogen, whilst with other metals this excess of tension is considerable, and the electrolysis is hence non-reversible; it is least for those metals which possess the greatest occlusion capability. Experiments on the electrolysis of solutions of potassium bromide or potassium iodide in *N* sulphuric acid proved that the precipitation of the bromine or iodine on platinum electrodes is reversible; this is also found to be the case for the precipitation of silver on silver electrodes in solution of silver nitrate, or of double cyanides.

L. M. J.

Magnetic Susceptibility of Inorganic Compounds. By STEFAN MEYER (*Ann. Phys. Chem.*, 1899, [ii], 69, 236—263).—The magnetic susceptibility of a number of inorganic compounds in the form of powder has been determined by the balance method previously employed in the case of elements (compare *Abstr.*, 1899, ii, 587). The molecular magnetism is the coefficient of susceptibility divided by the number of gram-molecules per litre of space. Experiments in which the field strength varied from 6000 to 10000 (C.G.S. units) showed that the coefficient of susceptibility, except for ferric oxide, is independent of the field strength.

A compound of two diamagnetic elements is always diamagnetic, and a compound of two paramagnetic elements is generally paramagnetic, but may be diamagnetic, as in the case of beryllium, magnesium and aluminium oxides, and silica. Oxygen always lowers the susceptibility of an element, and thus the oxides of paramagnetic elements may be diamagnetic; the lowering effect is greater the greater the proportion of oxygen atoms in the oxide. Besides chromium, manganese, iron, cobalt, and nickel, there is another series of strongly magnetic elements—lanthanum, cerium, praseodymium, neodymium, ytterbium, samarium, gadolinum, and erbium, arranged in order of increasing magnetic susceptibility. The susceptibility of erbium oxide is about four times that of ferric oxide. The molecular magnetism of paramagnetic com-

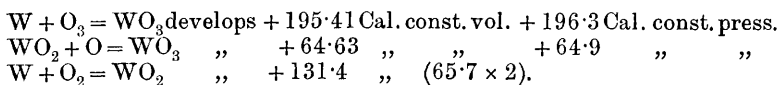
pounds is less than the sum of the atomic magnetisms of the components, as shown by the oxides of chromium, manganese, iron, cobalt, and nickel. For diamagnetic substances, the molecular magnetism is approximately additive. That the molecular magnetism is not purely additive is shown by the fact that the value for a hydrated salt differs from the value for the anhydrous salt by less than the amount calculated for the water of crystallisation.

The molecular magnetism of the halogen compounds of a metal increases with the atomic weight of the halogen, and a similar law holds for compounds of different alkali metals with the same halogen.

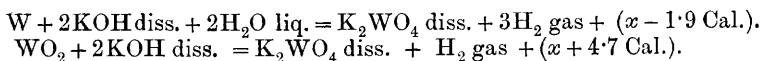
The connection between the atomic volume and the magnetic susceptibility of the elements is shown by an atomic volume curve. Strongly magnetic elements are found at the minima and the parts of the curve immediately preceding, the chief exception being oxygen which, however, behaves in compounds as if it were diamagnetic. Polonium and radium in their compounds are found to be paramagnetic, and thus these elements will probably find a place at minima of the atomic volume curve. The connection between atomic volume and magnetic susceptibility is confirmed by the fact that when the atomic volume decreases with fall of temperature, the susceptibility increases: further, in compounds where there is an increase of volume, the susceptibility decreases. J. C. P.

A Simple Protection for Fused-in Platinum Wires. By WILHELM PALMAER (*Ber.*, 1899, 32, 2570—2571).—Where a platinum wire has to be fused into the wall of a glass vessel, as is frequently the case in electrochemical apparatus, it is recommended to have only a very short piece of wire projecting outside the vessel; surrounding this wire is a small piece of narrow glass tubing fused on to the glass vessel. By pouring mercury into this glass tube, contact is made, and the danger of breaking the platinum wire or of splintering the glass around its point of entry is avoided. T. H. P.

Heat of Oxidation of Tungsten. By MARCEL DELÉPINE and L. A. HALLOPEAU (*Compt. rend.*, 1899, 129, 600—603).—When finely divided tungsten is burnt in oxygen in the calorimetric bomb, the heat liberated per gram is 1062 cal., whilst the dioxide WO_2 , under similar conditions, gives 299.2 cal. It follows that



The heat developed by combination with the successive atoms of oxygen is approximately the same, and is practically identical with the heat of oxidation of iron, which explains the interactions of water, tungsten, hydrogen, and tungstic anhydride at different temperatures. The results also explain the reactions of tungsten with various metallic oxides, the reduction of tungstic anhydride by certain metals only, and the reduction of mercuric, cupric, platinic, silver and gold salts by the red and blue tungsten oxides.



C. H. B.

A Simplification of Beckmann's Boiling Point Apparatus. By SAMUEL L. BIGELOW (*Amer. Chem. J.*, 1899, 22, 280—287).—To obviate the danger of superheating, and to secure a constant heating effect independent of changes of gas pressure, the author adopts as the source of heat a spiral of thin platinum wire immersed in the solvent and heated by means of an electric current of constant strength; the boiling vessel adopted is the same as in Beckmann's method, but is surrounded by a layer of felt to avoid cooling by radiation and convection. The electric connection to the heating wire is furnished by two glass tubes filled with mercury, passing through the cork and reaching nearly to the bottom of the vessel; through the lower ends of these are fused platinum hooks on which the heating spiral is suspended. The beads which are necessary in Beckmann's method to ensure uniformity of temperature and avoid superheating are not required with the new apparatus. Although, in general with electric heating, the results are normal, remarkably low values are obtained with very dilute solutions which point to dissociation occurring, "under the conditions of the experiment, of non-electrolytes in solvents to which it is not usual to ascribe dissociating power"; the author intends investigating this question.

W. A. D.

Relation between Pressure and Evaporation. By EDWIN H. HALL (*J. Physical Chem.*, 1899, 3, 452—456).—Nernst derives the equation of reaction isotherms from the consideration of a system in which a reaction proceeds in a given direction, and in which the concentration is maintained constant by the introduction and removal of the compounds reacting and produced in the states of solids or non-miscible liquids, and he assumes that the work required for this is zero. This necessitates equality of volumes, and the author hence introduces an additional term $P(V - V')$ and applies the altered equation to the case of a single liquid or solid in the presence of its gaseous phase. Expressions are thus obtained for the vapour density, as a function of external pressure, for water over ice at -10° and over liquid water at 0° .

L. M. J.

Density of Liquids and Saturated Vapours. By RUDOLF VON HIRSCH (*Ann. Phys. Chem.*, 1899, [ii], 69, 456—478).—The densities of toluene, *o*-xylene, *m*-xylene, *p*-xylene, propionic acid, normal and iso-butyric acids, both as liquids and saturated vapours, have been determined at 190° , 212° , 237° , and 276° , the boiling points of dimethylaniline, diethylaniline, isobutyl benzoate and bromonaphthalene respectively. The method adopted was essentially that of Young (*Trans.* 1891, 59, 37 and 911).

When D and d are the densities at a given temperature of liquid and saturated vapour respectively, the mean values $(D + d)/2$ for different temperatures lie on a straight line in all cases examined, in conformity with Matthias' law. The curve connecting density and temperature would thus naturally be a parabola, but the actual curve

is found to differ from the parabolic form in being flattened at the vertex.

The constants a and b of van der Waal's equation, calculated from the determined densities, are found to alter with the temperature, b slowly increasing and a generally diminishing with rising temperature; a increases with the temperature only in the case of p -xylene.

The author criticises the commonly accepted theory of the critical point, and considers illogical the view that the densities of liquid and vapour are equal at the critical temperature. The existence of a critical point is denied, for both liquid and vapour are regarded as having a critical density. From this point of view, van der Waal's assumptions that at the critical point $dp/dv=0$ and $d^2p/dv^2=0$ are not justified. J. C. P.

Phenomena of Effusion of Permanent Gases. By ROBERT EMDEN (*Ann. Phys. Chem.*, 1899, [ii], 69, 264—289 and 426—453).—When a gas issues under pressure from a narrow opening, stationary sound waves are formed in the jet. Photographs of the jet afford a means of measuring the wave-length and determining its variation with the size of aperture, with the pressure of the gas flow, and with the chemical nature of the gas. Experiments with air, carbon dioxide, and hydrogen show that, for a given size of aperture and a given gas pressure, the wave-length is independent of the molecular weight of the gas. J. C. P.

Van't Hoff's Equation and the Molecular Weights of Liquids. By CLARENCE L. SPEYERS (*J. Amer. Chem. Soc.*, 1899, 21, 725—732. Compare Abstr., ii, 1898, 213).—The equations $n/(N+n) = (p-p')/p$ and $n/N = (p-p')/p'$, where n and N are the number of gram-molecules of solute and solvent, p and p' the vapour pressures of solvent and solution respectively, give numbers agreeing well with observation, whilst the equation $n/N = l(p/p')$ is not at all in harmony with experiment, especially at higher concentrations. The molecular weight of acetic acid calculated by this formula from Linebarger's experiments on a mixture of benzene and acetic acid has quite absurd values. The author deduces the latter equation by a process similar to that employed by van't Hoff, but is unable to suggest any correction which would bring the formula into harmony with experiment. J. C. P.

A New Inorganic Dissociative Solvent. By PAUL WALDEN (*Ber.*, 1899, 32, 2862—2871).—Liquid sulphur dioxide has a remarkable power of dissolving the most varied substances, both inorganic and organic, the solutions often showing a characteristic colour: thus potassium, sodium, and ammonium iodides all dissolve readily, forming yellow solutions. Among soluble organic substances are benzene, naphthalene, ethyl alcohol, benzoic acid, phenol, ethyl acetate, aniline, diphenylamine, α - and β -naphthylamine. The solutions of diphenylamine and α -naphthylamine are blood-red in colour, that of β -naphthylamine is orange.

The fact that the dissolved substances react readily with each other

points to their being electrolytically dissociated: thus by double decomposition $KI + NH(CH_3)_3Cl = KCl + NH(CH_3)_3I$; all these substances are soluble in liquid sulphur dioxide except potassium chloride, which is accordingly precipitated. Ammonium thiocyanate and sublimed ferric chloride give a blood-red colour, exactly as in aqueous solution.

The conductivity of sulphur dioxide solutions is considerable, and in some cases greater than that of equally concentrated aqueous solutions. The increase of the molecular conductivity with dilution is irregular, and for the iodides much more marked than in their aqueous solutions. Ammonium salts in sulphur dioxide solution have a smaller conductivity than potassium or rubidium salt solutions of equal concentration: the conductivity of ammonium, tetramethylammonium, and tetraethylammonium iodides increases with the complexity of the positive ion. The difference between μ_{512} and μ_{16} for potassium iodide is greater in sulphur dioxide solution than in aqueous solution; hence both the degree of dissociation and the ionic velocities differ in the two solvents.

As a further test of the degree of dissociation, determinations of the molecular weight were carried out, the boiling point method being employed. The molecular rise of the boiling point of sulphur dioxide was calculated to be 15° , and with this constant the method gave normal and steady values for the molecular weights of naphthalene, toluene, and acetanilide. The iodides of potassium, sodium, rubidium, and ammonium give a value for the molecular weight which is nearly twice the normal value, whilst certain other salts, such as potassium thiocyanate and tetramethylammonium iodide, have approximately the theoretical molecular weight, thus behaving like non-electrolytes.

An explanation of this abnormal behaviour, which is to a certain extent analogous to that of liquid ammonia solutions (compare Abstr., 1899, ii, 202), is reserved until further investigations have been made.

J. C. P.

Nature of Colloidal Solutions. By K. STOECKL and LUDWIG VANINO (*Zeit. physikal. Chem.*, 1899, 30, 98—112).—The authors consider that colloidal metallic solutions consist of suspensions of extremely finely divided solid particles, and give the following reasons for their view. By boiling there is no continuous change in the boiling point, and the suspended material is almost completely precipitated after short boiling. Colloidal solutions bring about elliptic polarisation of light, which could be caused by solid particles, the diameters of which are smaller than the wave-length of the light, whilst, further, the colour of colloidal gold solutions is also explicable on the assumption that they contain small suspended particles. The electrical properties of these solutions and their behaviour to dialysers are also in accord with this view of their nature. The same reasoning may also be applied in the case of colloidal solutions of metallic sulphides.

L. M. J.

Function of the Medium in Chemical Change. By JULIUS WILHELM BRÜHL (*Zeit. physikal. Chem.*, 1899, 30, 1—63).—The velocity of the tautomeric change of ethyl mesityloxidoxalate from the enolic

to the ketonic form has been investigated in various solvents, and found to vary greatly with the nature of the latter (Abstr., 1899, ii, 735). The dissociative powers of solvents are closely associated with their dielectric constants (Abstr., 1894, ii, 266), and the same is found to obtain for their powers of inducing the above tautomeric change. No absolute proportionality exists, or can be expected, inasmuch as the dielectric constant varies greatly with temperature and also with the frequency of the electrical waves. This dissociative power is regarded as due to a form of energy which the author terms the "medial energy"; this, although not identical, is closely connected with the heat energy of the compound. The internal energy of a compound cannot be actually determined, since physical and chemical changes are only connected with changes of energy, but it is probable that it is greatest in compounds with the highest specific heat, and latent heat of fusion or evaporation. The examination of these constants for a large number of compounds indicates that high values are also generally associated with high dielectric constants and dissociative power. For the recognition and estimation of the tautomeric forms (chemical methods are not available, and cryoscopic methods are untrustworthy), the author considers the best methods to be the determination of the optical properties or the electrical conductivity.

L. M. J.

Gaseous Reactions in Chemical Kinetics. VI. and VII. By MAX BODENSTEIN (*Zeit. physikal. Chem.*, 1899, 30, 113—139).—The author gives a detailed account of the various thermostats used in his researches on gaseous reactions (Abstr., 1899, ii, 548, 637, 638, 639, 733). For vapour baths, sulphur, phosphorus pentasulphide, mercury, and diphenylamine were employed; for liquid baths, oil, lead, and an alloy of tin and lead. Temperatures were measured by mercury thermometers containing carbon dioxide under pressure, and by an air thermometer, and he considers the temperatures accurate to one degree. In summarising the results of the whole work, the author considers he has proved that gaseous reactions proceed continuously, and only at the absolute zero would an absolute inertness be reached, and hence that the assumption of a state of "false equilibrium" is erroneous. In the oxidation of phosphorus or phosphorus trihydride, the reaction apparently ceases at certain pressures of oxygen; in these cases, however, the reaction is very complicated, and the author does not consider that the supposition of a state of false equilibrium is necessitated (see also Duhem, Abstr., 1899, ii, 739).

L. M. J.

Application of the Equilibrium Law to the Formation of Oceanic Salt Deposits with Especial Reference to the Stassfurt Beds. II. Equilibrium Relations of Carnallite. By JACOBUS H. VAN'T HOFF and WILHELM MEYERHOFFER (*Zeit. physikal. Chem.*, 1899, 30, 64—88. Compare Abstr., 1898, ii, 564).—The authors have previously investigated the solubility curves for magnesium chloride, and the present paper contains an extension of this work to carnallite, but the diagrams and curves are necessary for the complete explanation of the results. Below zero, the following equilibrium points are obtained: -11.1° ice, potassium chloride, solution: -33.6° ice, magnesium

chloride dodecahydrate, solution: -34.3° , ice, potassium chloride, magnesium chloride dodecahydrate, solution. At -21° , carnallite is formed, being unstable in solution below this temperature, and from this point two curves branch, those for the solid phases (1) carnallite and potassium chloride, (2) carnallite and magnesium chloride. The latter curve has various transition points for the various hydrates of magnesium chloride in the presence of carnallite, these temperatures being different from those for the pure compound. At 152.5° , an upper limiting temperature for carnallite is reached, at which it decomposes into potassium chloride and magnesium chloride tetrahydrate. From the -21° transition point also proceeds the curve for the solid phase carnallite and potassium chloride to the temperature 167.5° , where the carnallite decomposes and melts. From this point to the previous decomposition point at 152.5° is another curve for the equilibrium of carnallite with potassium chloride, and the curve then proceeds as the solubility curve of magnesium chloride tetrahydrate in the presence of potassium chloride to the temperature of 176° , when a transition point to the dehydrated salt is reached. The solubility experiments were carried to 186° , and complete melting in sealed tubes was found to occur at 265° ; no evidence of any compound of the two chlorides other than carnallite was obtained. L. M. J.

Inorganic Chemistry.

Production of Ozone by the Decomposition of Water by Fluorine. By HENRI MOISSAN (*Compt. rend.*, 1899, 129, 570—573).—When fluorine is passed into water cooled at 0° , the liberated oxygen contains from 10 to 12 per cent., or, under the most favourable conditions, as much as 14.39 per cent., of ozone, and is decidedly blue. The proportion of ozone is higher the more rapid the current of fluorine, provided that the water is kept at 0° , and subject to the maximum limit of 14.39 per cent.; it is markedly less if the temperature of the water is allowed to rise.
C. H. B.

Hyposulphurous Acid. By ARNOLD NABL (*Monatsh.*, 1899, 20, 679—684).—If dry sulphur dioxide is passed into absolute alcohol in which metallic zinc is suspended, and contained in a flask from which air is excluded, a white precipitate is formed. This is left for a day, filtered, and the operation then repeated. The solution deposits small, microscopical, rhombic needles which, after drying in vacuum to eliminate the alcohol of crystallisation, give figures on analysis agreeing with the formula ZnS_2O_4 . The other product, insoluble in alcohol, appears to be a mixture.
R. H. P.

Isomerism of Salts of Ammonium, Hydroxylamine, and Hydrazine. By ALEXANDER P. SABANÉEFF [with A. DSHEWACHOFF, M. EFROSS, Z. GINSBURG, J. LEMKE, M. PROSIN, and A. WLASSOFF] (*Chem. Centr.*, 1899, ii, 32—33; from *J. Russ. Chem. Soc.*, 1899, 31, 375—383. Compare Abstr., 1898, ii, 577).—The following pairs of

isomeric compounds have been prepared and their molecular weights determined by Raoult's method: (1*a*) ammonium hydroxylamine hydrogen phosphite, (1*b*) diammonium hydrogen phosphate; (2*a*) hydroxylamine dihydrogen phosphite, (2*b*) ammonium dihydrogen phosphate; (3*a*) hydroxylamine formate, (3*b*) ammonium hydrogen carbonate; (4*a*) hydroxylamine acetate, (4*b*) ammonium glycollate; (5*a*) hydrazine oxalate, (5*b*) hydroxylamine oxamate; (6*a*) hydrazine succinate, (6*b*) hydroxylamine succinamate; (7*a*) hydroxylamine benzoate, (7*b*) ammonium salicylate; (8*a*) hydroxylamine *m*-aminobenzoate, (8*b*) hydrazine salicylate, $\text{C}_6\text{H}_4\text{O} \begin{array}{c} \text{C}_6\text{H}_4\text{O} \\ \text{C}_6\text{O}_2 \end{array} \text{N}_2\text{H}_6$.

(2*a*) is a syrup which, with absolute alcohol, yields hydroxylamine phosphate. (3*a*) crystallises in needles, and is easily soluble in water, forming an acid solution which decomposes on boiling, and does not then give the hydroxylamine reaction. (4*b*) is prepared by mixing glycollic acid with the calculated quantity of ammonia and evaporating in a vacuum; if an excess of ammonia is used, diammonium glycollate is formed; it separates in needles, is easily soluble in water, giving an acid solution from which the acid salt is obtained on evaporating. (5*a*) crystallises in needles, and is very slightly soluble in water. (5*b*) forms crystals, and is easily soluble in water. (6*a*) separates in very perfect crystals, and is soluble in water. (6*b*) gradually changes into hydroxamic acid; the same change is brought about by boiling the solution. (7*a*) is very slightly soluble in water. (7*b*) separates as the anhydrous salt when aqueous solutions of ammonia and salicylic acid are mixed and heated. (8*a*) is very slightly soluble in water, but more so in alcohol. (8*b*) is prepared from salicylic acid and hydrazine hydroxide. (2*a*), (3*a*), (4*a*), (5*b*), (6*b*), (7*a*), and (8*a*) are prepared from the barium salts of the corresponding acids and the sulphates of the nitrogen bases. Whilst measuring the electrical conductivity of hydrazine sulphate, its oxidation by platinum black was observed, and when oxygen is passed into an aqueous solution in which platinum black is suspended, the sulphate is completely oxidised, nitrogen, ammonium sulphate, sulphuric acid, and water being formed. E. W. W.

Action of Potassammonium on Arsenic. By C. HUGOT (*Compt. rend.*, 1899, 129, 603—605).—The action of excess of potassammonium on arsenic yields a brick-red compound, AsK_3NH_3 , analogous to that previously obtained from sodammonium (*Abstr.*, 1899, ii, 151), and when this is heated at 300° in a vacuum, it yields a black compound, AsK_3 . When the arsenic is in excess, the product is an orange solid, $\text{K}_2\text{As}_4\text{NH}_3$, which, when heated a little below 300°, yields a cinnabar-red compound, K_2As_4 . C. H. B.

The Atomic Weight of Boron. By HENRI GAUTIER (*Compt. rend.*, 1899, 129, 595—598).—Boron sulphide, B_2S_3 , prepared by the action of dry hydrogen sulphide on dry amorphous boron at a red heat, was decomposed by sodium hydroxide solution, oxidised with bromine water, and precipitated with barium chloride. Four experiments give $B = 11.041$ with a probable error ± 0.017 .

Boron carbide prepared in the electric furnace by the action of

sugar-charcoal on amorphous boron in presence of copper, was decomposed by chlorine, and the residual carbon weighed as such, and also in the form of carbon dioxide. Two experiments give $B = 10.997$.

C. H. B.

Atomic Weight of Boron. By HENRI GAUTIER (*Compt. rend.*, 1899, 129, 678—681. Compare Abrahall, *Trans.*, 1892, 61, 650; Ramsay and Aston, *Trans.*, 1893, 63, 207; Rimbach, *Abstr.*, 1893, ii, 207).—Boron tribromide, obtained by passing pure bromine over pure boron heated to a dull red heat, was fractionally distilled alone, and then finally over reduced silver, when it distilled quite constantly at 90.5° . Pure boron trichloride was obtained in a similar manner. A weighed quantity of the boron haloid was decomposed by water, and the halogen determined as silver haloid. The mean value obtained for the atomic weight of boron by nine experiments on the decomposition of the bromide was 11.021, with a probable error of ± 0.006 , and from five experiments on the chloride, 11.011, with a probable error of ± 0.008 . The mean of these values is 11.016, a number which the author adopts for the atomic weight of boron in preference to the values obtained by analysis of boron sulphide and boron carbide (compare preceding abstract).

H. R. LE S.

Graphite. By LUDWIG STAUDENMAIER (*Ber.*, 1899, 32, 2824—2834. Compare *Abstr.*, 1898, ii, 96; 1899, ii, 481).—When graphitic acid is heated with sulphuric acid and water at 180° , it gives an insoluble *pyrographitic acid*, which retains the form and appearance of the original graphite. When oxidised with nitric acid, this gives a soluble product containing mellitic acid, a red substance soluble in ether, a dark brownish-red substance soluble in alcohol, and a black residue insoluble in alcohol or ether. When treated with a mixture of fuming nitric acid and potassium chlorate, unlike ordinary pyrographitic acid, it gives a transparent, yellowish-green *pseudographitic acid*; this resembles graphitic acid but is more soluble, less stable, and more readily oxidised; it gives a black reduction product with stannous chloride.

T. M. L.

Treatment of Lepidolite. By JULIUS FORMÁNEK (*Chem. Centr.*, 1899, ii, 11—12; from *Oesterr. Chem. Zeit.*, 2, 309—312).—In order to obtain caesium and rubidium compounds from lepidolite, the finely powdered mineral is decomposed with concentrated sulphuric acid in an iron pan, and the solution evaporated in a lead vessel. The residue is taken up with water, and the potassium, caesium, and rubidium alums which separate are crystallised from water several times, and then treated with barium hydroxide. The excess of the baryta and most of the alumina are removed by means of carbon dioxide, and the solution, after neutralising with oxalic acid, is evaporated until crystals begin to form. Most of the potassium salt separates on cooling, and the rest is removed from the residue by fractional crystallisation, the caesium and rubidium salts being afterwards separated by the same means.

E. W. W.

Commercial Calcium Carbide. By HENRI MOISSAN (*Bull. Soc. Chim.*, 1899, [iii], 21, 865—871).—Theoretically, 1 gram

of calcium carbide should yield 349 c.c. of acetylene, the amounts obtained from seven commercial samples varied from 292·8—318·7 c.c.; three inferior specimens, which were grey and porous, instead of having a fused, crystalline structure, gave only 228·6, 250·4, and 260·3 c.c. respectively. The gas sometimes contains notable quantities of ammonia, and several specimens of carbide yielded a little hydrogen phosphide. To facilitate the study of the insoluble residue, the carbide was decomposed with an aqueous solution of sugar, whereby the lime produced is kept in solution. The residue consists principally of the silicides of carbon, calcium, and iron, sometimes mixed with a little graphite and calcium sulphide; dilute (10 per cent.) hydrochloric acid extracts iron, lime, and small quantities of aluminium and phosphorus; the concentrated acid dissolves further quantities of lime and silica, whilst carbon silicide and graphite remain unattacked. The various forms in which these impurities exist were recognised by microscopical examination. The *silicon* occurs chiefly as carbon silicide, but small quantities of calcium silicide, silica, and a compound containing iron, carbon, and silicon are also formed. Silicon hydride, from the decomposition of calcium silicide, is often evolved in the treatment with concentrated hydrochloric acid. The total *sulphur* in three samples of carbide was found to be 0·37, 0·43, and 0·74 per cent.; it exists as calcium sulphide and aluminium sulphide. Hydrogen sulphide is not liberated when impure calcium carbide is decomposed by water, since it is retained by the calcium hydroxide formed in the reaction; traces of a volatile organic compound containing sulphur seem, however, to be formed in some cases, since the gas, after being washed with potash and lead acetate solution, yields a small quantity of sulphuric acid when burnt. Iron is found as silicide and carbosilicide. Phosphorus occurs chiefly as calcium phosphide, but is also found combined with iron and silicon. Carbon is sometimes found as graphite retaining calcium and silicon; none was detected in the form of diamond.

N. L.

Action of Magnesium on Saline Solutions. By DONATO TOMMASI (*Bull. Soc. Chim.*, 1899, [iii], 21, 885—887).—When magnesium wire is placed in a solution of potassium chloride, the metal is converted into hydroxide, with liberation of hydrogen; the potassium chloride simply favours the oxidation of the magnesium, and is not itself decomposed. With ammonium chloride solution, a vigorous reaction occurs, hydrogen is evolved, and ammonium magnesium chloride formed. A 30 per cent. solution of calcium chloride attacks magnesium, slightly in the cold and more readily on heating, with the formation of magnesium hydroxide and hydrogen, but a saturated solution is without action unless the metal is finely divided and the liquid heated. A 30 per cent. solution of magnesium chloride has very little action on magnesium, but the boiling solution is easily decomposed by a magnesium-platinum couple, with the formation of magnesium hydroxide and oxychloride. The action on magnesium of solutions of various other salts was examined, and the products of the reactions, in addition to hydrogen, were found to be as follows. Sodium and lithium chlorides: magnesium hydroxide. Barium and strontium

chlorides: scarcely any action on magnesium. Cupric chloride: cuprous chloride, copper oxychloride, and magnesium chloride. Cadmium chloride: cadmium oxychloride, metallic cadmium, and magnesium chloride. Cobalt chloride: cobalt hydroxide and magnesium chloride. Lead chloride: lead oxychloride, metallic lead, and magnesium chloride. Mercuric chloride: mercurous chloride, mercury oxide, and magnesium chloride. Ferric chloride: ferric hydroxide, ferric oxychloride, and magnesium chloride; ferric chloride is not reduced by magnesium. Chromic chloride: chromium hydroxide and magnesium chloride. Platinic chloride: metallic platinum and magnesium hydroxide. Gold chloride: metallic gold, magnesium hydroxide, and magnesium chloride. Copper sulphate: metallic copper, cuprous hydroxide, basic copper sulphate, and magnesium sulphate; at 0° , cuprous hydroxide only is obtained. Zinc sulphate: metallic zinc, zinc hydroxide, basic zinc sulphate, and magnesium sulphate. Ferrous sulphate: ferrous hydroxide, and magnesium sulphate. Manganese sulphate: manganese hydroxide and magnesium sulphate. N. L.

Anhydrous Magnesium Carbonate. By RODOLPHE ENGEL (*Compt. rend.*, 1899, 129, 598—600).—When magnesium ammonium carbonate is gradually heated in a current of dry air at a temperature not exceeding $130\text{--}140^\circ$, it yields anhydrous magnesium carbonate which differs from the natural mineral, and from the carbonate prepared by Senarmont, but resembles that obtained by the action of heat on magnesium potassium sesquicarbonate (*Abstr.*, 1886, 821). It retains the crystalline form of the double carbonate, is very hygroscopic, sets like plaster when mixed with water, and absorbs almost instantly about 100 times its own volume of ammonia gas.

Attempts to prepare an ammonium magnesium sesquicarbonate gave negative results, and the compound, $\text{MgCO}_3 \cdot \text{NH}_4\text{HCO}_3 + 4\text{H}_2\text{O}$, ascribed to Favre, was never described by him. C. H. B.

Dicarbonyl Cuprous Chloride. By WILLIAM APP JONES (*Amer. Chem. J.*, 1899, 22, 287—311).—Carbonic oxide is not absorbed by dry cuprous chloride, but in presence of sufficient hydrochloric acid to form a thin paste, an amount of gas is absorbed at 0° which corresponds with the formation of *dicarbonyl cuprous chloride*, $\text{Cu}_2\text{Cl}_2 \cdot 2\text{CO} + 4\text{H}_2\text{O}$; on adding ice-water, white plates having this composition separate which rapidly decompose in the air. The compound prepared by passing carbonic oxide into cuprous chloride in presence of water or dilute hydrochloric acid ($1\text{HCl} : 2\text{H}_2\text{O}$) is not decomposed by diminishing the pressure until the latter is reduced to $135\text{--}125$ mm., when complete decomposition occurs; in presence of concentrated hydrochloric acid, decomposition begins at 410 mm. pressure and gradually increases as the pressure is reduced to 160 mm., when it takes place more rapidly and is complete at 130 mm. pressure. Curves are given showing these results.

On passing carbonic oxide into a solution of cuprous chloride in pyridine at 0° , the compound $2\text{Cu}_2\text{Cl}_2 \cdot 3\text{CO}$ appears to be formed, but could not be isolated; on raising the temperature, decomposition occurs

regularly, until at 100° it is nearly complete. The results are plotted in the form of a curve.

When oxygen is passed into dicarbonyl cuprous chloride at 0° , the latter is decomposed, giving rise to a small quantity of carbon dioxide; the formation of this cannot be due to increased activity of the oxygen brought about by the cuprous chloride undergoing oxidation, and thus splitting the molecular into atomic oxygen, for when a mixture of oxygen and carbonic oxide is passed through ferrous sulphate or chloride these compounds are oxidised, but no carbon dioxide is formed.

In discussing the decomposition of dicarbonyl cuprous chloride by reducing the pressure or raising the temperature, it is pointed out that this takes place similarly to that of compounds the "atomic" nature of which cannot be doubted; its properties are compared with those of other inorganic compounds containing carbonic oxide, and the conclusion is reached that it must be regarded as a true chemical compound.

The behaviour of dicarbonyl cuprous chloride with oxygen, chlorine, hydrogen, and nitrogen shows that, at the moment of its liberation from the compound, carbonic oxide possesses no increased chemical activity.

W. A. D.

Spectroscopic Analysis of Neodymium and of Praseodymium. By WILHELM MUTHMANN and L. STÜTZEL (*Ber.*, 1899, 32, 2653—2677. Compare Abstr., 1898, ii, 518; von Scheele, Abstr., 1898, ii, 519; 1899, ii, 291; Bettendorf, Abstr., 1890, 851).—According to Crookes' "one band one element" theory, praseodymium must contain 37 different elements, whereas according to von Scheele the substance is homogeneous. The authors themselves consider that the composite nature of praseodymium is probable, although not established, and that even if true the separation of the constituents, on account of the similarity in their chemical behaviour, presents an almost impossible task. Specimens of praseodymium from Bastnäs cerite and from Australian and Brazilian monazite have been compared with Shapleigh's preparations and no differences have been detected. The composite nature of neodymium is even still more in doubt, as, so far, pure neodymium has not been obtained; the product obtained by the sulphate method of separation contains 2 per cent. of praseodymium. A new separation by the aid of the chromates is quicker, and it is hoped will give better results.

Neodymium has the most complex absorption spectrum of all the earths, the number of bands in neutral chloride solution being 24. All these are not necessarily visible at the same time; in certain concentrated solutions, the six yellow bands become one, similarly for the green; on dilution, several groups disappear completely, particularly the narrow bands at the red end of the spectrum.

Numerous instances of change in the configuration of bands of the rare earths are known, but the causes have not been determined. A notable instance is found in the case of praseodymium; ordinary didymium gives the blue line λ 469 of praseodymium as a well-defined, not over broad, absorption band; when the earth is fractionated by Welsbach's

method, the line loses in intensity, broadens and moves towards the violet end of the spectrum ; on further fractionation, the band becomes smaller and more intense, but even in the purest specimens is never so sharp as in the crude didymium.

Bunsen (*Annalen*, 1866, 128, 190) pointed out that the bands in the spectra of didymium salts vary considerably, according to the nature of the acid constituent. Further variations have been found in the case of both praseodymium and neodymium. Neodymium nitrate and chloride give different absorption spectra, especially in the green part of the spectrum ; the nitrate in dilute nitric acid gives a single pale band about $\lambda = 522$, whereas in the chloride there are two bands, 525.5 and 521.5, and a pale band 520.5 ; the yellow bands in the chloride are sharper than in the nitrate.

Still greater differences are observed when the spectra of salts derived from carboxylic acids are examined. A solution of carbonate, probably containing the metal as the hydrogen carbonate, has not the characteristic dark red colour of the nitrate, but a fairly intense blue, due to the fact that the yellow absorption band has increased considerably in intensity, whilst the violet band λ 432—424 has completely disappeared ; the green bands are more pronounced than in the nitrate, and all bands are some 7.5 λ nearer the red end of the spectrum, and, in addition, a new orange band, $\lambda = 600.5$, has made its appearance.

Somewhat similar differences have been observed in the case of praseodymium, not merely does the relative luminosity of the bands vary with different salts, but also the order in which the lines disappear on diluting the solutions.

It is obvious that the absorption spectrum is not simply dependent on the molecular weight of the anhydrous salt, as Bunsen suggested.

The authors have employed a spectroscopic method for the estimation of praseodymium and neodymium, although, according to Schottländer (*Ber.*, 1892, 25, 569), this method is inapplicable. The observations were made with a special Krüss apparatus, and in calculating the results, Vierordt's equation, $A = c / -\log J$, was employed, where A = constant, c = concentration, and J = intensity of light after passing through a 10 mm. layer of the solution when the original intensity of the light = 1.

In the following minerals—orthite from Miask, cerite from Riddarhyttan, and orthite (allanite) from Llano Co., Texas, it was found that the percentage of neodymium was practically twice that of praseodymium.

J. J. S.

Radio-active Barium Salts and Polonium. By FRITZ GIESEL (*Ann. Phys. Chem.*, 1899, [ii], 69, 91—94).—The author has independently obtained from uranium ores other than pitchblende a substance, consisting chiefly of barium sulphate, which emits Becquerel rays. The substance is similar to that obtained by P. and S. Curie, according to whom it contains an active element radium.

Freshly crystallised barium salts containing radium are only slightly active, but in the course of a few days or weeks the activity increases to a maximum ; the portions which crystallise first are more active than

those subsequently obtained from the mother liquor. The chloride, bromide, and iodide phosphoresce without any previous illumination, especially when anhydrous; in moist air, they gradually lose this property, but renewed heating restores it to them. The stronger the phosphorescence of any particular specimen, the feebler is the emission of Becquerel rays. Barium platinocyanide, prepared from active barium chloride and potassium platinocyanide, shows strong, spontaneous phosphorescence, which grows less intense as time goes on, the green colour of the double salt changing to yellow and finally to brown. By dissolving and crystallising the brown product, the green salt can again be obtained. The active constituent of the barium salts has not been isolated, and it seems impossible to effect a separation by fractional crystallisation alone.

Strongly active products containing polonium are also being investigated. Hydrogen sulphide produces in them a precipitate which surpasses in activity the best barium salt preparation. The chloride prepared from this sulphur compound is equally effective, as is also the metal deposited from the chloride solution by metallic zinc or an electric current.

The penetrating power of polonium rays is much less than that of radium rays, and consequently the shadow produced by a hand or metallic object is much sharper and deeper with the former than with the latter.

J. C. P.

A New Radio-active Substance. By A. DEBIERNE (*Compt. rend.*, 1899, 129, 593—595).—The constituents of pitchblende which are not precipitated by hydrogen sulphide from an acid solution, but are precipitated by ammonia or ammonium sulphide, include a small quantity of a substance which emits radiations capable of acting on a photographic plate, making barium platinocyanide phosphorescent and accelerating the discharge of electrified bodies. Apart from its radio-activity, which seems to be about 100,000 times as great as that of uranium, it resembles titanium in general properties. It differs from radium in not being luminescent.

C. H. B.

Mineralogical Chemistry.

Dopplerite. By C. CLAESSEN (*Jahrb. f. Min.*, 1899, i, Ref., 424; from *Chem. Zeit.*, 1898, 523).—Analysis of dopplerite from an Oldenburg moor gave:

C.	H.	O.	Ash.	Total.
52.96	4.67	34.10	8.27	100.00

L. J. S.

New Zealand Coal and Ambrite; Barbados Manjak. By P. PHILLIPS BEDSON (*Trans. Fed. Inst. Mining Eng.*, 1899, 16, 388—390).—Coal from New Zealand gave analysis I (by A. Dodds); the composition of the dried ash-free coal is given under Ia; 10—13 per cent.

of the coal is soluble in pyridine. Ambrite, a brown, transparent resin, associated with this coal, gave II (Dodds). An asphalt from Barbados, locally known as manjak, gave III (by R. L. Treble); it resembles albertite in appearance, but is completely soluble in pyridine.

	Fixed carbon.	Volatile matter.	Moisture.	Ash.	S.
I.	46.44	47.80	4.66	1.10	0.54
II.	—	—	0.59	0.18	—
III.	36.52	61.90	—	1.58	—

	C.	H.	O.	N.
Ia.	74.32	5.67	20.01	
IIa.	80.95	9.87	9.18	—
IIIa.	81.18	8.43	10.39	—

L. J. S.

Identity of Binnite with Tennantite : Composition of Fahlerz. By GEORGE T. PRIOR and LEONARD J. SPENCER (*Min. Mag.*, 1899, 12, 184—213).—The small, brilliant crystals of “binnite” are of rare occurrence in the white, saccharoidal dolomite of the Binnenthal in Switzerland. They are cubic and hexakistetrahedral, and the formula usually assigned to them is $3\text{Cu}_2\text{S}_2\text{As}_2\text{S}_3$. It is now shown that they are crystallographically, physically and chemically identical with the less perfectly developed crystals of Cornish tennantite. Analysis I was made on eleven crystals (weighing 0.3101 gram), of which the streak is chestnut-brown; thin splinters are translucent and crimson by transmitted light. This analysis gives the formula $3\text{Cu}_2\text{S}_2\text{As}_2\text{S}_3 = \text{Cu}_3\text{AsS}_3$. Analysis II is of crystals, of which the streak is black, and which, in thin splinters, are opaque; formula $[3(\text{Cu}, \text{Ag})_2\text{S}_2\text{As}_2\text{S}_3] + \frac{1}{12}[6\text{FeS}, \text{As}_2\text{S}_3]$. The variation in the colour of the streak of the mineral depends on the amount of iron present.

Analyses I—V by G. T. Prior. In each case, detailed descriptions are given of the crystallographic and physical characters and of the associations of the material analysed.

	Cu.	Ag.	As.	Sb.	Bi.	Fe.	Zn.	Pb.	S.	Total.	Sp. gr.
I.	49.83	1.87	19.04	—	—	1.11	—	0.17	27.60	99.62	4.62
II.	44.12	4.77	[20.49]	—	—	3.68	—	—	26.94	100.00	4.598
III.	45.39	—	trace	28.85	—	1.32	—	0.11	24.48	100.15	4.921
IV.	41.55	—	trace	28.32	0.83	1.02	2.63	0.62	24.33	99.30	4.969
V.	30.56	15.26	trace	27.73	—	3.51	trace	0.05	23.15	100.26	5.047

The results of these analyses of “binnite,” as well as the published analyses of Cornish tennantite, differ considerably from the figures required by the accepted formula for fahlerz (tetrahedrite and tennantite), namely, $4\text{R}''\text{S}, \text{R}'''\text{S}_3$, where $\text{R}'' = \text{Cu}_2, \text{Ag}_2, \text{Fe}, \text{Zn}$, and $\text{R}''' = \text{As}, \text{Sb}, \text{Bi}$. Very few of the published analyses of fahlerz agree with this formula, and minerals which have given the formula $3\text{R}''\text{S}, \text{R}'''\text{S}_3$ have often received new names. Three new analyses were therefore made of specially pure tetrahedrite crystals free from copper pyrites, blende and pyrites which are usually so intimately associated with fahlerz; the fracture of these crystals was smooth and conchoidal and with a brilliant lustre.

Analysis III is of material from a large crystal of octahedral habit from "Fresney d'Oisans, Dauphiné"; the streak is dark brown; after deducting the iron as pyrites, the formula is $3\text{Cu}_2\text{S}, \text{Sb}_2\text{S}_3 = \text{Cu}_3\text{SbS}_3$. Analysis IV is of the well-known brilliant crystals from Horhausen, in Rhenish Prussia; very thin flakes are crimson by transmitted light, and the streak is dark brown. Analysis V is of tetrahedral crystals, probably from Wolfach, Baden; the streak is black. IV and V give the formula $[3(\text{Cu}, \text{Ag})_2\text{S}, \text{Sb}_2\text{S}_3] + \frac{1}{10}[6(\text{Fe}, \text{Zn})\text{S}, \text{Sb}_2\text{S}_3]$.

These analyses suggest the new formula $3\text{R}'_2\text{S}, \text{R}''_2\text{S}_3 + x[6\text{R}'''\text{S}, \text{R}''_2\text{S}_3]$, where $\text{R}' = \text{Cu}, \text{Ag}$; $\text{R}'' = \text{Fe}, \text{Zn}$; $\text{R}''' = \text{As}, \text{Sb}, \text{Bi}$; and x is a small fraction, often $= \frac{1}{10}$ and $\frac{1}{5}$, but rising to $\frac{1}{2}$ in the case of the highly ferri-ferous tetrahedrite "coppite." In this formula, the group $(\text{Fe}, \text{Zn})_6\text{S}_6$, and not $(\text{Fe}, \text{Zn})_3\text{S}_3$, is isomorphous with Cu_6S_3 . Only in those cases where iron and zinc are absent does the simple formula $3\text{R}'_2\text{S}, \text{R}''_2\text{S}_3$ hold good.

Numerous previous analyses are discussed and found to agree with the new formula. L. J. S.

Melonite (?), Coloradoite (?), Petzite and Hessite. By WILLIAM F. HILLEBRAND (*Amer. J. Sci.*, 1899, [iv], 8, 295—298).—*Melonite*?—Impure material from the Melones mine, in the Mother Lode region, California, gave the results under I; after deducting a little hessite and tellurium, this gives the formula NiTe_2 . In colour and cleavage, the material agrees with Genth's melonite from the same locality; Genth, however, gave the formula Ni_2Te_3 .

Coloradoite?—One small specimen from the Norwegian mine in the same district showed dolomite, petzite, hessite, and a mercury telluride, which is probably coloradoite.

Petzite.—Analysis of pure material from the Norwegian mine gave II, agreeing with the formula $\text{Au}_2\text{Te}, 3\text{Ag}_2\text{Te}$.

Hessite.—Material from San Sebastian, Jalisco, Mexico, gave analysis III; sulphur, iron and zinc are also present.

	Te.	Ni.	Ag.	Au.	Se.	Mo.	Pb.	Total.	Sp. gr.
I.	80.75	18.31	0.86	—	—	—	—	99.92	—
II.	33.21	—	41.87	25.16	trace	0.08	—	100.32	8.925.
III.	36.11	—	61.16	—	—	—	1.90	99.17	8.24.

L. J. S.

Langbeinite from the Punjab Salt Range. By FREDERICK R. MALLETT (*Min. Mag.*, 1899, 12, 159—166).—A potassium magnesium sulphate occurring as a lenticular stratum in the 'kallar' (impure rock salt) of the Mayo mines, Punjab, India, was discovered and analysed in 1873. The material has now been more completely examined, and found to be the same as the cubic mineral langbeinite, $2\text{MgSO}_4, \text{K}_2\text{SO}_4$, recently described from the Prussian salt deposits (*Abstr.*, 1898, ii, 168).

The Indian mineral is associated with salt, sylvite and kieserite, and sometimes encloses these. It is colourless and transparent, and optically isotropic. Sp gr. 2.84; $H=4$. The powder is slowly but completely soluble in water. Analysis gave:

K ₂ O.	MgO.	SO ₃ .	NaCl.	H ₂ O.	Total.
22·23	19·08	57·27	0·41	0·84	99·83

On exposure to the air, the powder absorbs water, and there is an increase in weight of nearly 57 per cent. ; the decomposition therefore takes place in accordance with the equation : $2\text{MgSO}_4, \text{K}_2\text{SO}_4$ (langbeinite) + $13\text{H}_2\text{O} = \text{K}_2\text{SO}_4, \text{MgSO}_4, 6\text{H}_2\text{O}$ (picromerite) + $\text{MgSO}_4, 7\text{H}_2\text{O}$ (epsomite).

Langbeinite, as isotropic octahedra, may be artificially produced by fusing together magnesium and potassium sulphates in the proper proportions.

L. J. S.

Formation of Oceanic Salt Deposits, particularly of the Stassfurt Beds. XIII. Evaporation of Sea Water at 25°. By JACOBUS H. VAN'T HOFF and W. MEYERHOFFER (*Chem. Centr.*, 1899, ii, 76 ; from *Sitzungsber. Akad. Wiss. Berlin*, 20, 372—383).—The most recent and trustworthy analyses of sea water show that on an average 1000 parts contain NaCl, 47 ; KCl, 1·03 ; MgCl_2 , 7·36 ; and MgSO_4 , 3·57. When sea water is evaporated at 25°, the salts separate out in the following order :—(1) NaCl ; (2) NaCl + $\text{MgSO}_4, 7\text{H}_2\text{O}$ and NaCl + $\text{MgSO}_4, 6\text{H}_2\text{O}$; (3a) NaCl + $\text{MgSO}_4, 6\text{H}_2\text{O}$ + KCl and NaCl + $\text{MgSO}_4, 5\text{H}_2\text{O}$ + KCl ; (3b) NaCl + $\text{MgSO}_4, 4\text{H}_2\text{O}$ + $\text{MgCl}_2, \text{KCl}, 6\text{H}_2\text{O}$; (4) NaCl + $\text{MgSO}_4, 4\text{H}_2\text{O}$ + $\text{MgCl}_2, \text{KCl}, 6\text{H}_2\text{O}$ + $\text{MgCl}_2, 6\text{H}_2\text{O}$, and in the following relative quantities :

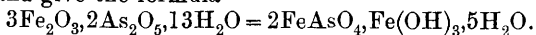
	NaCl.	MgSO_4 .	KCl.	MgCl_2 .	$\text{KCl}, 6\text{H}_2\text{O}$.	MgCl_2 .
1.	94·5					
2.	2·39	1·63				
3a.	0·59	1·42	0·72			
3b.	0·50	0·22		1·27		
4.	0·02	0·30		0·07	6·02	

These quantities, however, are only obtained when the separate crystallisations are removed from the mother liquor. E. W. W.

Pharmacosiderite. By ERNALD G. J. HARTLEY (*Min. Mag.*, 1899, 12, 152—158).—The formula of pharmacosiderite is uncertain ; it is based on an analysis by Berzelius (1824), and no analysis has since been made. The present analyses were made on selected green crystals from Cornwall ; sp. gr. 2·798. A green crystal placed in ammonia solution very soon becomes red throughout without alteration of the optical characters ; on placing such a red crystal in dilute hydrochloric acid, the green colour is restored to the whole crystal. Two preliminary analyses (I and II) show a deficit, which was afterwards found to be due to the presence of potassium. This element is present in all the Cornish specimens examined, but in variable amount (2·68 and 4·12 per cent. K₂O), and in two specimens from Hungary only traces were found. About 10 per cent. of water is lost at 100° ; at 130°, the crystals begin to turn brown and opaque, and about 14·18 per cent. is lost (= $5\text{H}_2\text{O}$ in the formula given below). A complete analysis is made on another specimen is given under III.

	As ₂ O ₅ .	P ₂ O ₅ .	Fe ₂ O ₃ .	K ₂ O.	H ₂ O.	Total.
I.	37·53	2·04	39·29	—	19·63	98·49
II.	36·85	2·06	38·81	—	[19·63]	97·35
III.	37·16	1·20	37·58	4·54	18·85	99·33

The ratios between the iron, arsenic acid and water are fairly constant, and give the formula



The potassium is assumed to replace hydrogen in the hydroxyl, and the formula is finally written as $2\text{FeAsO}_4, \text{Fe}[\text{O}(\text{H}, \text{K})]_3, 5\text{H}_2\text{O}$. L. J. S.

[Chabazite] from North Carolina. By JULIUS H. PRATT (*Jahrb. f. Min.*, 1899, i, Ref. 229—231; from *Jour. Elisha Mitchell Sci. Soc.*, 1897, 14, 61—83).—Analyses by C. Baskerville are given of the small crystals of chabazite associated with wellsite (Abstr., 1897, ii, 565) in the Buck Creek corundum mine, Clay Co., North Carolina. The simple and twinned rhombohedra occur on felspar, hornblende and corundum. The material for analysis was separated into two portions by means of a heavy liquid; anal. I on material of sp. gr. 2.147—2.203; II of sp. gr. 2.203—2.244.

	SiO ₂ .	Al ₂ O ₃ .	FeO.	CaO.	BaO.	MgO.	K ₂ O.	Na ₂ O.	H ₂ O.	Total.
I.	45.08	19.68	2.00	7.22	0.18	0.23	4.34	3.35	18.00	100.08
II.	46.15	20.74	2.00	6.92	0.24	0.22	4.10	3.35	16.30	100.02

This variation in composition and specific gravity supports Streng's hypothesis as to the composition of chabazite.

Other minerals from North Carolina, described in this paper, have already been noticed (Abstr., 1898, ii, 342, 606). L. J. S.

Constitution of Pectolite, Pyrophyllite, Hemimorphite and Analcite. By FRANK W. CLARKE and GEORGE STEIGER (*Amer. J. Sci.*, 1899, [iv], 8, 245—257).—In continuing the investigation of the constitution of natural silicates, special importance is attached to the two following reactions: (1), when talc is ignited there is a liberation of one-fourth of the silica (Abstr., 1890, 948); this suggests that other acid metasilicates may behave in a similar way; (2), dry ammonium chloride, at its temperature of dissociation, acts differently on different minerals (Abstr., 1892, 772).

Pectolite.—The material used in the experiments was from Bergen Hill, New Jersey; analysis gave the results under I, agreeing with the accepted formula $\text{HNaCa}_2\text{Si}_3\text{O}_9$. Only a small portion of the water is given off below a dull red heat. After igniting the mineral, sodium carbonate solution takes up 8.68 per cent. of silica, or one-sixth of the total amount. This, it is considered, indicates that the mineral is an acid metasilicate as expressed by the above formula. Before ignition, sodium carbonate solution, or even distilled water, has a slow, decomposing action on the mineral, both silica and bases being withdrawn; the action is, however, not one of simple solution.

Pyrophyllite.—The material used was from Deep River, North Carolina, and gave the results under II. The empirical formula, AlHSi_2O_6 , is apparently that of an acid metasilicate, but after ignition, only about 2 per cent. of silica is liberated. The formula is therefore written as $\text{OH} \cdot \text{Al} : \text{Si}_2\text{O}_5$, that is, as a basic salt of the acid $\text{H}_2\text{Si}_2\text{O}_5$. The mineral is very slightly attacked when heated with dry ammonium chloride.

Hemimorphite.—White material from Franklin, New Jersey, gave the results under III. The formula generally accepted represents the

mineral as a basic metasilicate, $\text{SiO}_3(\text{Zn}\cdot\text{OH})_2$. Here the hydrogen is all combined in one way, and so, too, is the zinc. In all other possible formulæ, the hydrogen, as well as the zinc, must be represented as present in at least two modes of combination. Several experiments were made with the idea of extracting a definite fraction of the zinc or water, but the results were negative and only tend to support the usual formula. Water and sodium carbonate solution have very little action either before or after ignition of the mineral. By heating with dry ammonium chloride, all the zinc is converted into zinc chloride.

Analcite.—Crystals from Wasson's Bluff in Nova Scotia gave analysis IV. The water is lost as follows :

Temperature.	100°.	180°.	260°.	300°.	Low redness.	Full redness.	Blast.	Total.
H ₂ O per cent.	0·58	1·16	3·64	1·57	1·90	0·11	nil	8·96

Before or after ignition very little silica is extracted by sodium carbonate solution. Heated at 350° with dry ammonium chloride, about half of the sodium is converted into chloride, and ammonia is retained ; this ammonia is not given off when the residue is warmed with caustic sodium solution. The composition of the residue, after extracting sodium chloride, is given under V, which agrees approximately with $\text{H}_2\text{Na}_2\text{Al}_4\text{Si}_8\text{O}_{24}\cdot\text{NH}_3$. This ammonia derivative suggests that the analcite formula should be quadrupled, namely, $\text{Na}_4\text{Al}_4\text{Si}_8\text{O}_{24}\cdot 4\text{H}_2\text{O}$. G. Friedel has previously shown that the water of analcite may be replaced by ammonia (Abstr., 1896, ii, 481).

An excess of silica over that required by the accepted analcite formula, $\text{NaAlSi}_2\text{O}_6\cdot\text{H}_2\text{O}$, is shown by analysis IV and by some previous analyses. This is explained by analcite being, not a metasilicate, but a mixture of ortho- and tri-silicate, the general formula being $\text{NaAlX}_2\cdot\text{H}_2\text{O}$, where $\text{X} = n\text{SiO}_4 + m\text{Si}_3\text{O}_8$. This explains the alteration of albite, $\text{NaAlSi}_3\text{O}_8$, and nephelite, NaAlSiO_4 , to analcite. For normal analcite, the formula is finally written as $\text{Al}_4\text{Na}_4(\text{SiO}_4)_2(\text{Si}_3\text{O}_8)_2\cdot 4\text{H}_2\text{O}$. This is written structurally to show the relation between analcite, leucite and the garnet-sodalite group.

	SiO ₂ .	Al ₂ O ₃ .	Fe ₂ O ₃ .	CaO.	Na ₂ O.	H ₂ O.	Total.
I.	53·34	0·33	—	33·23	9·11	2·97 ; MnO, 0·45 ; CO ₂ , 0·67	100·10
II.	64·73	29·16	0·49	—	—	5·35 ; TiO ₂ , 0·73 ; MgO, trace	100·46
III.	24·15	0·19		0·12	—	7·95 ; ZnO, 67·55	99·96
IV.	57·06	21·48	0·13	0·16	12·20	8·96	99·99
V.	62·59	24·34	—	0·18	8·11	2·32 ; NH ₃ , 2·46	100·00

L. J. S.

Analysis of Rocks. By ERNST A. WÜLFING (*Ber.*, 1899, 32, 2214—2224).—Analyses are given of four samples of Keuper marl from the neighbourhood of Tübingen ; some were made by the author, the others by Dittrich. The agreement is fairly close, except in the case of alumina and ferric and sodium oxides. The author separated the iron and aluminium by running the nearly neutral solution of the chlorides into excess of a boiling solution of caustic soda (made from the metal), and found more alumina and less ferric oxide than Dittrich, who fused the mixed oxides with pure caustic soda in a silver crucible ; the discrepancy in the sodium is unexplained.

Stress is laid upon the necessity that the reagents used in a rock-analysis, including the distilled water, should be pure. C. F. B.

Experimental Petrology. By K. BAUER (*Jahrb. f. Min.*, 1899, Beil. Bd. 12, 535—580).—In continuing the experiments of Doelter and Schmutz (Abstr., 1897, ii, 54, 329) on the artificial production of rocks, the main object has been to test whether different rocks can be formed from the same magma. Powdered rocks—mica-schist, granite, diorite, phonolite, leucite-lava, nepheline-basalt and andesite, or mixtures having the same composition as these—were fused in a platinum crucible with various fluxes. The following will serve as an example of the several experiments made. A mixture consisting of mica schist, potassium fluoride, sodium fluoride, calcium fluoride, sodium tungstate and potassium tungstate was maintained in a fused condition at 1400° for two hours, in a plastic condition for seven hours, and allowed to cool slowly for five hours. Under the microscope, the product resembled a mica-andesite, and was seen to contain plagioclase, biotite, augite, magnetite, scapolite, nepheline and glass. The same mica-schist with other fluxes gave a product resembling a melilite-basalt. Using diorite with various fluxes, the products were quartz-basalt, andesite, melilite-basalt, mica-andesite and phonolite-pitchstone. Phonolite-pitchstone was also produced from mixtures having the compositions of granite and of phonolite. This is taken to indicate that different rocks may be formed from the same magma, and *vice versa*. [The chemical composition of the magmas have, however, been considerably modified by the large amount of fluxes used.]

Hornblende was formed in three of the fusions, whilst quartz was formed only once. L. J. S.

[**Mineral Analyses**]. By W. TARASSENKO (*Jahrb. f. Min.*, 1899, i, Ref., 458—475; from *Mem. Kieff Naturalists' Soc.* (Russian), 1896, 15, 1—347).—The following mineral analyses are given in a petrological paper on the gabbro and allied rocks in the districts of Radomysl, gov. Volhynia, and Shitomir, gov. Kieff, Russia.

Orthoclase (micropertthite) in a labradorite-rock from Poromowka, Shitomir district, gave anal. I; the material analysed contained spindle-shaped enclosures of plagioclase.

Labradorite from the same rock gave II and III; the former of sp. gr. 2·692—2·686; the latter of sp. gr. 2·686—2·677; this material also contained spindle-shaped enclosures, possibly of orthoclase.

Diallage in a labradorite-rock from Kamenny Brod, Radomysl district, gave IV (also MnO, trace; X, 0·15).

	SiO ₂ .	TiO ₂ .	Al ₂ O ₃ .	Fe ₂ O ₃ .	FeO.	CaO.	MgO.	K ₂ O.	Na ₂ O.	H ₂ O.	Total.
I.	62·58	0·59	20·83	—	—	2·10	—	12·24	2·08	0·41	100·33
II.	54·78	0·36	28·16	0·27	0·48	10·35	—	1·45	4·84	0·04	100·73
III.	55·32	0·28	28·16	0·05	0·52	10·05	—	0·97	5·20	0·03	100·58
IV.	50·11	1·01	1·69	1·15	15·61	15·10	13·68	—	—	0·65	99·15

L. J. S.

Trap-rock of Rocky Hill, New Jersey. By ALEXANDER HAMILTON PHILLIPS (*Amer. J. Sci.*, 1899, [iv], 8, 267—285).—A dyke of dolerite in the Triassic strata at Rocky Hill, New Jersey, shows, in its width of half a mile, variations in chemical composition and in structure. Analysis I is of the microcrystalline rock at the margins; III is of the most coarsely crystalline material towards the centre of the dyke, and II is of an intermediate rock. Analyses are also given of material separated from the rocks by means of heavy solutions. IV and V are of the diallage from the rocks II and III respectively. VI and VII are of felspar (plagioclase) from the rock II, the former of sp. gr. >2.69, and the latter of sp. gr. <2.69. VIII and IX are of felspar, sp. gr. >2.69 and <2.69, from rock III; and X is of felspar (anorthoclase), of sp. gr. <2.60 from the same rock.

	SiO ₂	TiO ₂	Al ₂ O ₃	Fe ₂ O ₃	FeO	MnO	CaO	MgO	Na ₂ O	K ₂ O	P ₂ O ₅	H ₂ O	Total
I.	51.46	1.06	13.98	2.66	8.92	—	10.49	7.59	4.75	0.17	—	—	101.08
II.	50.34	1.56	15.23	2.82	11.17	0.14	9.61	5.81	2.93	1.02	0.20	0.26	101.09
III.	56.78	1.44	14.33	5.76	9.27	0.25	5.26	1.58	3.43	1.75	0.36	0.43	100.64
IV.	47.72	—	3.44	5.93	18.34	—	11.40	12.89	0.86	0.37	—	—	100.95
V.	48.54	—	5.50	2.77	21.25	—	10.97	7.67	3.10	—	—	0.82	100.62
VI.	53.84	—	29.30	0.81	—	—	10.08	0.28	5.31	1.16	—	0.44	101.22
VII.	62.26	—	21.87	0.54	—	—	6.53	0.15	7.98	1.20	—	0.32	100.85
VIII.	66.84	—	17.98	2.60	—	—	4.02	0.48	5.46	1.72	—	0.72	99.82
IX.	71.68	—	15.02	2.48	—	—	3.86	0.12	5.52	1.37	—	—	100.05
X.	66.28	—	16.79	1.60	—	—	0.71	0.13	9.76	5.31	—	0.49	101.07

L. J. S.

Analyses of Italian Volcanic Rocks. By HENRY S. WASHINGTON (*Amer. J. Sci.*, 1899, [iv], 8, 286—294).—Five analyses are given of trachytes from the Phlegrean Fields and from Ischia. L. J. S.

Meteoric Iron from Caperr, Patagonia. By LAZARUS FLETCHER (*Min. Mag.*, 1899, 12, 167—170).—This iron was known before 1869 in the neighbourhood of Caperr, Río Senguerr, Patagonia. It weighs 114 kilograms, and measures 48 × 31 × 27 cm. The structure is octahedral, and the etched surface shows distinct Widmanstätten figures with kamacite, tænite and plessite. Schreibersite is embedded in the kamacite. No troilite or silicate was seen. Sp. gr. 7.837. Analysis gave :

Fe.	Ni.	Co.	P.	Cr.	Cu.	S.	Total.
89.87	9.33	0.53	0.24	trace	trace	nil.	99.97

In composition and structure, this iron resembles the Joel iron from Atacama. L. J. S.

Cliftonite and Tænite in the Youndegin Meteoric Iron. By LAZARUS FLETCHER (*Min. Mag.*, 1899, 12, 171—174).—Cliftonite is the name given by the author to cubic crystals of graphitic carbon obtained from the meteoric iron found in 1884 in the sub-district of Youndegin, Western Australia. From a fragment weighing 8.32 grams, three milligrams of cliftonite were isolated (*Abstr.*, 1888, 30). More recently, a larger mass (97.25 grams) of the same iron was dissolved in dilute hydrochloric acid, but no cliftonite was seen. The cliftonite is there-

fore localised in one or more parts of the mass, and not uniformly distributed through it.

During the solution of the iron, thin, lustrous, black plates (total weight, 0.0870 gram) were set free; they appeared to be an alloy of nickel and iron belonging to the tænite group. After being kept for eleven years in a weighing tube, the material had increased in weight and altered in character owing to the formation of a layer of magnetic iron oxide on the surface. Sp. gr. 6.75. An analysis shows the material to be tænite, with the composition: Fe, 61.87; Ni(Co), 38.13. Phosphorus, copper and magnesium were also present in small amount. L. J. S.

Fluorine in the Mineral Waters of Portugal and Spain. By ANTONIO J. FERREIRA DA SILVA and ALBERTO D'AGUIAR (*Bull. Soc. Chim.*, 1899, [iii], 21, 887—890. Compare Abstr., 1899, ii, 501, 602, 675).—The general question of the presence and detection of fluorine in mineral waters is discussed. The Campilho spring at Vidago has been found by one of the authors to contain fluorine equivalent to 0.000942 gram of sodium fluoride per litre, a result which may be compared with the corresponding figures for the Gerez spring (0.02288) and for the Spanish mineral waters of Lugo (0.0242) and Guitiriz (0.0234). According to Gil, the presence of fluorine in many alkaline and sulphurous waters has hitherto been overlooked, owing to the fact that the tests usually applied for this element depend on the formation of hydrogen fluoride, whereas, since silica or silicates are also commonly present, it is rather silicon fluoride which is produced and should be sought for. N. L.

Physiological Chemistry.

Autodigestion of the Pancreas. By S. PFÖRRINGER (*Virchow's Archiv*, 1899, 158, 126—147).—Previous authors have called attention to the possibility of self-digestion being a cause of pancreatic cysts and necroses. Chiari (*Zeit. Heilk.*, 1896, 17), in particular, has directed attention to the fact that the pancreas is often found partially digested after death, and he considers that this may begin in the last hours of life. The present investigation confirms Chiari's views; it contains records of a hundred autopsies; the pancreas was examined microscopically, and evidence of digestive necrosis was found in forty-five, and this was very marked in eleven cases. The conditions of the patients (age, disease, &c.) appear to be as varied where such necrosis is found as in those cases where it is not found. W. D. H.

Action of Arginine on the Tryptic Digestion of Proteid. By D. LAWROFF (*Zeit. physiol. Chem.*, 1899, 28, 303—306).—The presence of arginine is helpful to the tryptic digestion of proteid. This appears to be connected with its alkalinity; an equivalent amount of sodium carbonate acts similarly. Arginine, like sodium carbonate, aids the

emulsification of fats; excess of arginine, as of sodium carbonate, is harmful. W. D. H.

The Fluorine in Tooth- and Bone-ash. By HEINRICH HARMS (*Zeit. Biol.*, 1899, 38, 487—498).—Fresenius' method with certain small modifications is well adapted for the detection of quite minimal quantities of fluorine. The amount of fluorine in bones and teeth as given by Carnot, T. Wilson, and Gabriel is much too great. The amount varies from 0.022 to 0.005 per cent. The variations in the amount of fluorine, as compared with the other constituents of the ash, which are fairly constant, show that the fluorine is not chemically combined with these, but is rather an accessory constituent; this view is confirmed by the presence in the bone of microscopic crystals of calcium fluoride. W. D. H.

Composition of the Cartilage of the Shark. By GUSTAV VON BUNGE (*Zeit. physiol. Chem.*, 1899, 28, 300—302).—The cartilage removed from the fish *Scymnus borealis*, which had been packed in ice, gave the following analytical results: water, 92.8 per cent.; organic material, 5.9; inorganic material, 1.3.

Of the inorganic material, sodium and chlorine were the most abundant constituents; details are also given of the other inorganic constituents.

Petersen and Soxhlet (*J. pr. Chem.*, 1873, [ii], 7, 181) state that the fresh cartilage contains 16.7 per cent. of sodium chloride; their specimen, however, had been packed in salt. W. D. H.

Substances present in the Liver which are converted into Sugar by Acids. By JOSEF SEEGEN (*Chem. Centr.*, 1899, ii, 58; from *Centr. Physiol.*, 13, 115—120. Compare *Abstr.*, 1898, i, 619).—After liver-extract has been heated with hydrochloric acid, more sugar is found than corresponds with the sugar and glycogen contained in the extract. The substance prepared from liver-extract by means of 90 per cent. alcohol contains nitrogen, reduces alkaline copper solutions, and, when heated with acids, yields a sugar with reducing properties, but the quantity so obtained is far too little to account for the excess of sugar formed from the extract by acid, hence the liver must contain yet another compound which is easily converted into sugar. The carbohydrate groups of the albumin are supposed to be affected by the action of the liver in such a way that they easily form sugar by the action of hydrochloric acid.

E. W. W.

Amount of Urea in the Liver. By RUDOLF GOTTLIEB (*Chem. Centr.*, 1899, i, 1298; from *Arch. expt. Path. Pharm.*, 42, 238—249).—See this vol., ii, 57.

Human Bile. By RICHARD VON ZEYNEK (*Chem. Centr.*, 1899, ii, 213—214; from *Wien. klin. Woch.*, 12, 568—569).—The quantity of bile secreted in a day amounts to 300—400 grams, containing 7—12 grams of solid matter; it is strongly alkaline, and has a sp. gr. 1.011—1.012. The bile pigments are completely precipitated by basic

lead acetate, but only partially by the normal salt ; the bile acids, mucin, and the colouring matter are thrown down by saturating with ammonium sulphate. Only a slight precipitate is formed by supersaturating with magnesium sulphate. Hydrochloric or sulphuric acid gives an amorphous precipitate and the liquid becomes deep green and gradually deposits the bile acids. Bile gives a yellow coloration with alkalis ; this is shown best by samples which have become of a greenish tinge by exposure to the air. The precipitate obtained by means of alcohol, when rubbed with glycerol, is capable of converting starch into sugar, but does not digest albumin. The bile secreted by the patient during each hour of a day was examined and found to be of a sp. gr. 1.011 and to contain in 1000 parts, 21.88 of solids, 2.39 of mucin, 13.8 of alkali salts of the bile acids, 8.96 of soluble salts, and 0.23 of insoluble salts. Another sample had a sp. gr. 1.012 and yielded 30.76 of solids, 2.087 of mucin, 18.31 of alkali salts of the bile acids, 0.78 of lecithin, 2.307 of cholesterol and fat, 9.10 of soluble salts, 0.31 of insoluble salts, 0.054 of ammonia and trimethylamine, and 2.087 of acid ethereal extract. On one day when 336.73 grams of bile were secreted, the solid residue amounted to 10.69 grams ; the amounts of the former per hour varied from 2.01 to 30.25 grams, and of the latter from 0.054 to 0.99 gram. The ash is principally made up of sodium chloride, the insoluble portion containing traces of iron and copper.

By adding zinc chloride and excess of ammonia to a very dilute aqueous solution of bile, a green coloration is formed in $\frac{1}{2}$ —1 hour, and the liquid shows a characteristic band in the red part of the spectrum about 650 $\mu\mu$ wave-length. Human urine containing bile pigments and bilirubin also give this reaction. E. W. W.

Degradation of Caffeine in the Organism of the Dog. By MARTIN KRÜGER (*Ber.*, 1899, 32, 2818—2824).—On administering 50.5 grams of caffeine during a period of 20 days to a dog which was fed exclusively on flesh, there was found in the urine excreted during this period 7.4 grams of 4:6-dimethylxanthine (theophylline), 6.6 grams of unchanged caffeine, 4.61 grams of 4-methylxanthine, 1.9 grams of 1:4-dimethylxanthine (theobromine), and about the same quantity of 1:6-dimethylxanthine (paraxanthine)—per 100 grams of caffeine originally administered. For the method of separation adopted, the original paper should be consulted. The results obtained show that all three methyl groups of caffeine are attacked simultaneously, and that the group in position 1 offers least resistance to elimination ; so that theophylline is the principal initial degradation product of caffeine, just as 4-methylxanthine is the principal product in the case of theobromine (Krüger and Schmidt, following abstract). The small quantity of theobromine obtained, taken in conjunction with Krüger and Schmidt's results, explains why heteroxanthine (1-methylxanthine) is not formed by the degradation of caffeine, and suggests that the 4-methylxanthine isolated owes its origin to theophylline rather than to theobromine. It is pointed out that theophylline and theobromine have hitherto never been isolated in the animal organism, but only from plant extracts. W. A. D.

Decomposition of Theobromine, Paraxanthine, and 4-Methylxanthine in the Animal Organism. By MARTIN KRÜGER and PAUL SCHMIDT (*Ber.*, 1899, 32, 2677—2682. Compare Albanese, *Abstr.*, 1899, ii, 777).—Bondzynski and Gottlieb's experiments (*Abstr.*, 1895, i, 434) have been repeated. Theobromine, when introduced into the bodies of dogs or rabbits, is excreted in the urine partly in an unaltered condition, but mainly as 1- and 4-methylxanthine. Paraxanthine is converted in the body of rabbits into 6-methylxanthine, identical with that found in human urine. Neither 1-methylxanthine nor xanthine could be isolated.

Although theobromine is converted into 1-methylxanthine in the animal system, attempts to obtain xanthine from 4-methylxanthine were abortive.

The separation of the purine derivatives from urea was accomplished by precipitating them with sodium hydrogen sulphite and copper sulphate; the purine derivatives obtained from the copper precipitate were treated with manganese peroxide in dilute acetic acid solution in order to destroy uric acid (compare *Abstr.*, 1898, i, 699).

J. J. S.

Intestinal Absorption and Saline Cathartics. By GEORGE B. WALLACE and ARTHUR R. CUSHNY (*Pflüger's Archiv*, 1899, 77, 202—209. Compare *Abstr.*, 1898, ii, 442).—Höber (*ibid.*, 74, 346) describes the absorption of saline solutions in the small intestine as depending on purely physical factors. This theory is opposed to the results previously published by the authors; the present paper restates their views, and adds some further confirmatory experiments.

W. D. H.

Passage into the Urine of Chloroform administered by Inhalation. By DIOSCORIDE VITALI (*L'Orosi*, 1899, 22, 145—148).—From the results of tests made on the urine of four patients before and after the administration of chloroform, the conclusion is drawn that chloroform does not pass into the urine. The presence in the urine of organic chlorine compounds produced from the chloroform could not be detected.

T. H. P.

Excretion in Blood-free and in Fasting Frogs. By WACŁAW VON MORACZEWSKI (*Pflüger's Archiv*, 1899, 77, 290—310).—The excreta from a number of normal fasting frogs kept in a clean vessel were collected, and in them the nitrogen, phosphorus, chlorine, ammonia, potassium, sodium, calcium, and magnesium were estimated. The results are given in full and compared with what occurs in frogs whose blood had been replaced by an iso-osmotic solution of sodium chloride; in these animals, which often live a considerable time, the metabolic changes are slow as evidenced by the reduction in the various substances excreted and mentioned above. When sodium nitrate is used instead, the amount of nitrogen is high from the excretion of nitrates, but the amount of potassium and sodium is high also. Sodium acetate is more fatal. Sodium sulphate raises the excretion of nitrogen, but the other substances are diminished, as when sodium chloride is used.

If a urea solution is substituted for the blood, there is an increase in the excretion of nitrogen, and of some of the other substances also. If sugar solution is used, the frogs stand it exceedingly well; all excretion diminishes except that of calcium; this probably depends on the ready solubility of calcium phosphate in solutions of sugar.

Frogs can stand considerable dilution of their blood without interference with nitrogenous metabolism. W. D. H.

Fat of Normal and of Degenerated Heart Muscle. By W. LINDEMANN (*Zeit. Biol.*, 1899, 38, 405—418).—The question always arises in connection with fatty degeneration, whether the fat is produced from proteid in the cells, or whether it has been merely transported from other parts and stored there. The comparison of the heart-fat in cases of fatty degeneration, mostly from cases of anæmia, with that in normal hearts, and with that in other parts of the body, appears to support the former view. The following table summarises the results obtained: column 1 gives the acid number, column 2 the saponification number; column 3 the iodine number, and column 4 the Reichert-Meissl number.

	1.	2.	3.	4.
Degeneration fat	18.35	257.4	108.5	23.9
Normal heart fat	7.3	202.3	61.1	2.0
Kidney and subcutaneous fat ...	3.76	201.8	70.8	0.9

The degeneration fat, in its high saponification number and large percentage of volatile fatty acids, resembles butter fat and the fat in the so-called tears of marine mammalia. W. D. H.

[Physiological Action of] **Acetonedicarboxylic Acid and Citric Acid.** By LUIGI SABBATANI (*Chem. Centr.*, 1899, ii, 22—23; from *Atti Real. Accad. Torino*, 34).—Experiments on dogs and rabbits show that the stupefying effect of acetone is not shared by citric, acetonedicarboxylic, or acetoacetic acids, which are only injurious in large doses. When acetonedicarboxylic acid is administered to healthy animals, it is partly decomposed in the stomach with liberation of carbon dioxide, but only very small quantities of acetone or of unchanged acid are found in the urine. Citric acid, under similar conditions, does not yield ketonic acids, or at most traces which escape detection in the urine.

Acetone may be separated from acetoacetic acid, ethyl acetoacetate and acetonedicarboxylic acid by the following method. Insoluble bromine compounds, such as ethyl $\alpha\alpha$ -dibromoacetate, pentabromoacetone, &c., are precipitated from the urine acidified with sulphuric acid by adding a slight excess of bromine water and allowing the mixture to remain 12 hours. The acetone itself is not attacked, and is distilled from the filtrate after removing the excess of bromine by means of powdered iron. Its amount is then determined by means of Lieben's method of conversion into iodoform. The amount of acetone, together with that derived from the ketonic acids, is similarly estimated in the liquid obtained by directly distilling a second portion of the acidified urine. Acetoacetic acid cannot be separated from ethyl acetoacetate, or acetonedicarboxylic acid by this method. E. W. W.

Chemistry of Vegetable Physiology and Agriculture.

[Effect of Mineral and Nitrogenous Nutritive Matters on the Fermenting Capacity of Yeasts.] By R. KUSSEROW (*Bied. Centr.*, 1899, 28, 630—632; from *Brennerei-Zeit.*, 1897, 14, Nos. 318—320; and *Centr. Bakt. Parasit.*, 1898, 4, ii, 154).—Addition of superphosphate, potassium phosphate, and magnesium sulphate increases the productive power of yeast in bad mash-material. Yeast distilleries should employ lower mash temperatures, to avoid separation of proteids with phosphates; in thick mash distilleries, the temperatures should be higher in order to separate froth-producing proteids, and to convert peptones and albumoses, as far as possible, into amides.

N. H. J. M.

Yeast. By CARL BÖTTINGER (*Chem. Zeit.*, 1899, 23, 313 and 645).—Solutions of grape sugar (5—6 per cent.) to which yeast was added were treated with lime (0.25 to 2 per cent.), with copper sulphate (0.17—1 per cent.), and with both substances together. In every case, there was a partial or complete destruction of the sugar in a few days, either with or without evolution of gas. With glycollic acid (0.33 per cent.) all the sugar fermented with abundant liberation of carbon dioxide. With glyoxylic acid, the production of carbon dioxide was only slight and soon ceased; further addition of yeast induced renewed liberation of gas, and in 30 days nearly half of the sugar was recovered; oxalic acid was found to be present. Pyruvic acid acts similarly to, but less energetically than, glyoxylic acid, and gives rise to an intense odour of *Lotus*. Further experiments were made with paraldehyde, acetone, acetic acid, benzaldehyde, tartaric, citric, and oxalic acids.

As regards the effect of sugar on the fermentation of grape juice, it was found that addition of 10 per cent. of grape sugar delayed the production of mould. In both cases, evolution of gas was very limited, and on distilling on the 20th day, there was only enough alcohol produced, both with and without sugar, to allow of detection by the iodoform test. The effect of sugar was rather physical than chemical.

N. H. J. M.

A Sugar Bacterium. By H. MARSHALL WARD and JOSEPH REYNOLDS GREEN (*Proc. Roy. Soc.*, 1899, 65, 65—84).—The bacterium occurs along with at least one yeast in a mixture of organisms said to have come from Madagascar, where it occurs as an “excrecence on the sugar cane.” The clumps induce vigorous fermentation in sugar solutions (15—20 per cent.), liberating relatively enormous amounts of carbon dioxide and some acid; oxygen is not necessary in any quantity.

The bacterium will practically only grow in presence of sugar, and only certain sugars are suitable: sucrose (after undergoing inversion) is far the best, lævulose is utilised to a slight extent, and dextrose is not a favourable medium. Dextrin, maltodextrin, maltose, lactose,

and soluble starch are all unsuitable or useless. Negative results were also obtained with glycerol and yeast extract, starch treated with diastase, potato, carrot, and milk.

In order to throw some light on the rôle of the bacterium and the yeasts respectively in the fermentation produced by the mixed organisms, a number of experiments were made in which different solutions (such as sucrose, a mixture of sucrose and lævulose, dextrose, &c.) were sown with pure cultures of (1) the yeast, (2) the bacterium, (3) the yeast and bacterium separately, and (4) the yeast and bacterium as ordinarily associated. It was found that production of alcohol was due to the yeast alone, the bacterium being without influence. The acid (acetic and succinic) was produced mainly by the bacterium; of the two acids relatively more acetic acid was produced by the bacterium than succinic acid. In sucrose, and in dark brown sugar containing lævulose, the conjoint organism produced less acids than the bacterium alone, whilst in dextrose the contrary was the case.

The presence of the bacterium is of no advantage, but rather disadvantageous to the yeast, whilst the yeast is of use to the bacterium in excreting nitrogenous food. The bacterium does not affect alcohol like ordinary acetifying organisms, and seems to act directly on the sugar with production of acid, the immediate antecedent of which is probably lævulose.

In sucrose, the bacterium produces a viscous material containing two carbohydrates in many respects similar to, but not quite identical with, Scheibler's dextran.

N. H. J. M.

Permanent Forms of Nitric and Nitrous Organisms. By ALFRED BEDDIES (*Chem. Zeit.*, 1899, 23, 645—647).—Sterilised solutions containing the nutritive substances present in manure heaps, the percentage of nitrogen being raised to 3 per cent. by the addition of ammonium sulphate, in which the alkalinity was made suitable by the addition of sodium carbonate or of phosphoric acid, were inoculated with soil. After being kept for several weeks in diffused light at 20—25°, the cultures in which nitrification was complete were employed for inoculating a fresh nutritive substance containing 1 per cent. of a strong solution of humus and 0.25 per cent. of sodium silicate.

Cultivations of nitrifying organisms prepared in this manner proved to be much less sensitive than those obtained by Winogradsky in absence of organic matter. Four stable varieties of nitric and three varieties of nitrous bacteria were isolated. The strongest form of the nitric bacterium resisted the action of steam at 100° for 2 minutes; and one form of nitrous bacterium lived for 1 minute in steam at 100°. Nitric and nitrous bacteria can be cultivated together and do not interfere with each other, and an inoculating material was prepared by drying previously sterilised calcareous soil to which both forms had been added.

Pot experiments are described in which grasses and cereals were grown in sterilised sand to which sterilised humus, ammonium sulphate, and minerals were added, with and without the addition of the inoculating material. With inoculation, the growth was stronger and more luxuriant.

Evidence was obtained that, in presence of an abundance of nitrifying organisms, denitrification is hindered and there is no loss of free nitrogen. When, however, denitrifying organisms predominate, the nitrifying bacteria are injured, especially if aëration is limited.

N. H. J. M.

Germination of the Carob Bean (*Ceratonia Siliqua*): Production of Mannose by a Soluble Ferment. By EMILE BOURQUELOT and HENRI HÉRISSEY (*Compt. rend.*, 1899, 129, 614—616).—In the germination of the carob bean, a soluble ferment is produced which acts on the albumin in the seed and produces from it mannose and galactose. Since saliva does not act on this albumin, it follows that the ferment in question is distinct from diastase. This is the first instance of the production of mannose by a soluble ferment (compare *Abstr.*, 1899, i, 839, 968).

C. H. B.

Action of Anæsthetic Vapours on the Vitality of Dry and Moist Seeds. By HENRI COUPIN (*Compt. rend.*, 1899, 129, 561—562).—The germinating power of the seeds of wheat and clover is not in the least affected by exposure, in the dry state, to the saturated vapour of ether or chloroform for 680 hours. These liquids may therefore be safely used for the destruction of insects in grain, and are to be preferred to carbon disulphide, which has an injurious action on some seeds, such as wheat. Experiments with white lupin, purple clover, hairy spring vetch, buckwheat, wheat, barley, maize, and hemp show that moist seeds are much more susceptible to the action of anæsthetics. In an atmosphere containing 1 c.c. of ether per 10 litres, germination takes place as usual; with a larger quantity of ether, growth is more or less retarded, purple clover being the most resistant of the seeds examined, and with 3·7 c.c. of ether per 10 litres all the seeds are killed, and will not germinate even when removed from the action of the ether and washed well with water.

N. L.

Absorption of Water and Dissolved Substances by the Stems of Plants. By ÉMILE BRÉAL (*Ann. Agron.*, 1899, 25, 449—458).—The absorption of different substances by plants was effected by inserting in the stems glass tubes drawn out to a suitable size, containing the solutions.

Whilst nitrates can accumulate in plants, it was found that ammonium salts, although absorbed, are soon converted into other substances. Nitrates accumulated abundantly in the stems, but could not be detected in the roots. Potassium humate was absorbed by lupins, and was afterwards visible when the stems were cut open. In the case of maize, it was observed that absorption of potassium humate resulted in the destruction of the nitrates present. Potassium humate, in conjunction with ammonium phosphate, diminished the amount of nitrate in amaranth without causing its entire disappearance; in the case of lupins, all the pre-existing nitrate disappeared.

N. H. J. M.

Food-stuffs of the Leaves of the Plane-tree and their Migration during the Growth and Decay of the Leaves. By G. M. TUCKER and BERNHARD TOLLENS (*Ber.*, 1899, 32, 2575—2583).—The leaves examined were picked at intervals during the summer; 500

being taken on each occasion; to obtain comparable results, only the two oldest leaves on any one twig were selected. After weighing and measuring the surface of an average sample, the leaves were dried, burnt, and the ash analysed, the constituents determined being SiO_2 , $\text{Fe}_2\text{O}_3 + \text{Al}_2\text{O}_3$, CaO , MgO , P_2O_5 , SO_3 , K_2O , Na_2O , Cl , and N .

The results show that the weight and also the amount of ash of the leaves increased until the leaves died, and then slightly decreased. The amounts of silica and lime show a similar behaviour, but the chlorine and sulphuric acid show a continuous increase, leaves plucked in November containing three times as much sulphuric acid as those plucked in June. Those constituents regarded as the more important food-stuffs show a quite different behaviour; the phosphoric acid and the potash increase very slightly until the leaves die, after which they diminish to less than half their original amounts. The amount of nitrogen steadily falls, having at the end a value less than one-fourth of the initial value.

Young leaves gathered in November show the presence of large quantities of potash, phosphoric acid, and nitrogen, the amounts of which are sufficient to account for the loss in these constituents suffered by the older leaves after death; any backward motion of these food-stuffs from the leaves to the stem or wood of the twigs the authors regard as of small amount.

Comparative experiments with leaves protected from rain and others non-protected show that rain has little, if any, washing-out action on the food stuffs of the leaves. T. H. P.

The Replacement of Potassium Salts by Rubidium Salts in Lower Fungi. By OSCAR LOEW (*Bied Centr.*, 1899, 28, 646—647; from *Bot. Centr.*, 1898, 74, 202—205).—Whilst the author has shown that rubidium can take the place of potassium in putrefaction bacteria, yeast, and *Penicillium*, the results of Günther's experiments indicate that such substitution can take place to some extent in *Botrytis cinerea*, but not in *Rhizopus nigricans*. The experiments now described confirm Günther's observation that differences exist in the case of various fungi as regards the power of utilising rubidium.

Bacillus coli develops equally well in the presence of rubidium and of potassium; *B. pyocyaneus* grows twice as quickly in the presence of potassium as with rubidium. *Cladothrix* failed to develop in the presence of rubidium, whilst a moderate growth was obtained with potassium (the organic food was 1 per cent. dextrose and 0.5 per cent. sodium acetate). N. H. J. M.

Yellow Colouring Matters accompanying Chlorophyll and their Spectroscopic Relations. By C. A. SCHUNCK (*Proc. Roy. Soc.*, 1899, 65, 177—186. Compare Abstr., 1899, ii, 540).—Alcoholic extracts of healthy green leaves contain two yellow colouring matters: (1) chrysophyll which separates in lustrous, red crystals, usually in minute quantities, and (2) an amorphous substance to which the author would restrict the name xanthophyll. This is obtained by spontaneous evaporation of the solution, after removing the chlorophyll by means of animal charcoal, and is impregnated with much

fatty matter. Another yellow colouring matter sometimes occurs with the xanthophyll; this gives no absorption bands, but only an obscuration in the violet and ultra-violet portion of the spectrum. Other yellow colouring matters may exist, but xanthophyll seems to predominate, and is also the principal yellow colouring matter of autumn leaves.

The absorption spectrum of chrysophyll consists of three bands, that of xanthophyll of four bands, in the violet and ultra-violet portions. The author concludes that the spectrum of crude chlorophyll (four bands in the less refrangible region and three in the violet) are due to chlorophyll alone, and not, as usually supposed, in part to the accompanying yellow colouring matters. Phyllocyanin and phylloxanthin have bands in positions identical with the three chlorophyll bands in the violet part of the spectrum. N. H. J. M.

Wheat. By GEORGE B. FRANKFOTER and E. P. HARDING (*J. Amer. Chem. Soc.*, 1899, 21, 758—769).—The germ of wheat was found to contain on the average 11·6 per cent. of oil. The sp. gr. of the oil is 0·9292 at 15° and 0·9374 at 0°. At 0°, the oil is a cloudy semi-solid, at 15° it is milky, and at 100° it becomes reddish-brown. When dried at the ordinary temperature, it increases slightly in weight during the first 45 days, and loses rather more during the next 30 days. The index of refraction of the oil when purified is 1·48325, 1·47936, and 1·47447 at 20°, 30°, and 40° respectively. As regards solubility, 1 gram of the oil dissolves in 1 c.c. of ether, 1 c.c. of chloroform, 30 c.c. of absolute alcohol, or 250 c.c. of 90 per cent. alcohol. The saponification value, according to Köttstorfer's method, is 188·83 mg. of KOH to 1 gram of oil. Iodine number (Hübl) 115·64. Acid value, 40·7. Five determinations of glycerol gave an average percentage of 7·35. The oil contains 2·0 per cent. of lecithin and 2·47 (mean of 5 analyses) of paracholesterol. The elaidin method gave 1·8 and 2·2 per cent. of paracholesterol. N. H. J. M.

Constituents of Chicory. By JULES WOLFF (*Chem. Centr.*, 1899, ii, 211—212; from *Ann. chim. anal. appl.*, 4, 157—162, 187—193).—The root of *Cichorium Intybus* contains inulin, $6C_6H_{10}O_5 + H_2O$, but no starch. The inulin obtained from the aqueous extract of the root by precipitating with 90 per cent. alcohol has a specific rotatory power $[\alpha]_D -36·57^\circ$ (Lescœur and Morelle) and does not reduce Fehling's solution. It is completely inverted by boiling for 20 minutes with 5 c.c. of hydrochloric acid, and the lævulose formed may be estimated by reduction or polarimetrically. An optically inactive sugar, *lævulin* or *synanthrose*, which does not reduce Fehling's solution, is also present, and is decomposed by hydrochloric acid into dextrose and lævulose. Chicory only contains a very small quantity of a sugar which reduces Fehling's solution directly, and this is probably lævulose derived from the inulin. The sugars are practically unchanged by drying the root, but by roasting, the quantity of reducing sugars which consist mainly of lævulose with some dextrose is increased, a large portion of the inulin is changed, and caramel and dextrin are formed.

The inulin contained in chicory may possibly be of use as a food in

cases of diabetes. The fresh root contains about 13—15 per cent. and commercial chicory from about 11—16 per cent. of inulin. Analyses of the fresh root, the dried material, and samples of commercial chicory are quoted.

E. W. W.

Constituents of Flores Kosso. By IWAN L. KONDAKOFF (*Arch. Pharm.*, 1899, 237, 481—493).—An historical account of previous investigations, serving as an introduction to the following abstract (compare especially, Flückiger and Buri, *Abstr.*, 1875, 468; Levin, *Diss.*, St. Petersburg, 1892; Leichsenring, *Abstr.*, 1894, i, 424; Dacomo and Malagnini, *Abstr.*, 1899, i, 158).

C. F. B.

Kossin or Taeniin of Pavesi and Vée. By IWAN L. KONDAKOFF and N. SCHATZ (*Arch. Pharm.*, 1899, 237, 493—507).—*Flores Kosso*, the female flowers of *Hagenia abyssinica*, are used as a vermifuge; the sample examined contained moisture 10·5 and ash 10·3 per cent. The flowers were treated with lime, 90 per cent. alcohol, and water, after the method of Pavesi (*Journ. Pharm. d'Amers*, 1858, 472) and Vée (*Neues Rep. Pharm.*, 8, 325); the alcohol was distilled off from the extract, and the residue decomposed with acetic acid, when kossin separated. When a solution of kossin in cold acetic acid or in alcohol is allowed to remain, crystals of kossin separate. If a solution of kossin in caustic alkalis is acidified with phosphoric acid, or a solution in baryta water decomposed with carbon dioxide, an amorphous variety of kossin, melting at 142°, separates; probably kossin contains a good deal of this.

The ethereal extract of another sample of the flowers contained (a) an amorphous substance mixed with (b) another substance, which was insoluble in cold alcohol, and formed crystals melting at 63°, (c) an amorphous substance, characterised by acid and reducing properties, and melting at 155—157°; (d) a wax-like substance, melting at 55°; (e) a resinous substance, and (f) kosotoxin. The latter amounted to 6 per cent. of the dry extract (which itself formed 4·7 per cent. of the drug). As regards kosotoxin, Leichsenring's results were not entirely confirmed; the melting point is 76°; the molecular formula, as determined by analysis and cryoscopically, is $C_{25}H_{32}O_9$, and the acid formed, in addition to kossin, when kosotoxin is boiled with 5 per cent. aqueous barium hydroxide, is not wholly a butyric acid, but contains another acid (valeric?) admixed.

The residue left after extraction of the flowers with ether yielded to alcohol an amorphous tannin, the amorphous substance (a), kosotoxin, and other substances which were not separated.

C. F. B.

Detection of Sulphur Dioxide in the Atmosphere of the Tharandt Forest. By HANS WISLICENUS (*Bied. Centr.*, 1899, 29, 643—644; from *Tharandt forst. Jahrb.*, 1898, 173—184).—Experiments made by the Ost process from May to October in different parts of the forest, at a distance of 10 kilometres from any source of smoke, showed the presence of sulphur dioxide inside the forest, although in less quantity than at the edges. The results of previous experiments indicate, however, that in consequence of the limited amount of light in the forest the sulphurous acid is comparatively harmless.

N. H. J. M.

Maize as Food in Servia. By ALEXANDER ZEGA and R. MAJSTOROVIĆ (*Chem. Zeit.*, 1899, 23, 544—545).—Maize is the most important food in Servia, and in some districts nothing else is used. Besides boiled and roasted maize, different kinds of bread (including "famine bread," an inferior kind in which carrots, nettles, &c., are employed as well as maize), cakes, and other kinds of food, and a beverage, prepared from maize meal and wheat bran, are described. Maize meal (1) yellow, and (2) white, has the following composition :

	Water.	Nitrog. subst.	Fat.	Carbo- hydrates.	Sugar.	Crude fibre.	Ash.	P ₂ O ₅ .
1.	12·69	10·11	4·23	67·44	2·70	1·43	1·40	0·74
2.	13·36	9·56	4·84	66·36	2·68	1·72	1·48	0·68

The composition of the various foods is given.

N. H. J. M.

Determination of the Action of some new Foods on the Secretion of Milk, with Special Reference to the Amount of Fat in the Rations formed with these Foods. By EBERHARD RAMM and W. MINTROP (*Bied. Centr.*, 1899, 28, 614—616 ; from *Milchzeit.*, 1898, No. 33).—The following conclusions are drawn from the results of the feeding experiments. A high percentage of fat in food does not result in higher percentage of fat in milk, but the different concentrated foods, in rations differing very little in composition, produced considerable variations in the percentage of fat in the milk (2·327—3·437).

As regards the various foods, it was found that cocoa-molasses (cocoa-husk meal mixed with molasses) was consumed in large amounts and, in conjunction with oil-cake rich in proteids, increased the yield of butter-fat above the average. Maize bran had no injurious effect on the health of the cows, even when consumed in large quantities. Blood molasses (blood, molasses, and offal of cereals) in quantities of 6—8 kilos. was not injurious, was in every respect favourable to milk secretion, and is a very valuable food for cows.

N. H. J. M.

Value of various Concentrated Foods. By WALDEMAR VON KNIERIEM (*Bied. Centr.*, 1899, 28, 616—618 ; from *Landw. Jahrb.*, 1898, Heft. 3 and 4).—The constituents of cocoa-nut cake show, according to results obtained with rabbits, the following percentage digestibility : crude protein, 95·7 ; crude fat, 99·1 ; crude fibre, 89·1 ; non-nitrogenous substance, 95·2. With a ram, the results were very similar (except in the case of crude fibre) to those obtained by Kühn with bullocks. The cake is one of the best concentrated foods. Hemp cake causes indigestion with rabbits as well as with sheep and horses ; it can, however, be given to cows in conjunction with considerable amounts of roots, potatoes, malt-germs, or brewers' grains, and is of importance in the feeding of young cattle. Sunflower cake gave lower results with rabbits than those given by Wolff, which were obtained with sheep. Rape cake in small quantities favours the digestion of non-nitrogenous constituents ; in the case of cows, it must be employed with care to avoid indigestion, especially when the cake develops mustard oil. Palm cake resembles cocoa-nut cake and is chiefly useful in promoting milk production.

N. H. J. M.

In Feeding with Sesamé Cake, do Substances which give the Baudouin Reaction appear in the Butter? By H. WEIGMANN (*Bied. Centr.*, 1899, 28, 629—630; from *Milchzeit.*, 1898, 529).—Experiments with cows in which sesamé cake was given in increasing quantity (up to 3 kilos. per day) showed that the butter was quite free from sesamé oil.

In examining butter for sesamé oil, it is important to employ only 0·1 c.c. of 1 per cent. furfuraldehyde solution; with 1 per cent. sesamé oil or 10 per cent. margarine, the coloration appears at once, whilst any other coloration can only appear in the course of about half an hour. The results obtained by Scheibe (*Milchzeit.*, 1897, 745) and Siegfeld (*Bied. Centr.*, 1899, 28, 415), which are opposed to those just described, are attributed to the employment of unsuitable amounts of furfuraldehyde, and to the correct conditions as to time and temperature not having been observed. N. H. J. M.

Alkali Soil in Montana. By FRANK W. TRAPHAGEN and W. M. COBLEIGH (*J. Amer. Chem. Soc.*, 1899, 21, 753—757).—The bare patches of soil incrustated with white, red, or yellow salt which occur in Montana, and are known as “alkali” soils, are of two kinds, the “white,” consisting mainly of sodium sulphate, and the “black,” of sodium carbonate. The appearance of the latter is due to the solvent action of the carbonate on humus which, on evaporation, is left as a shiny black coating on the surface. As little as 0·1 per cent. of sodium carbonate at the surface is deleterious, whilst crops will thrive in the presence of as much as 0·6 per cent. of “white alkali.” Larger quantities of white alkali are injurious rather by interference with the process of osmosis than through any chemical action.

Analyses of different soils and crusts are given, showing that the amounts of soluble salts differ widely; there is, however, a very constant relation of the amounts of different salts in the extracts. In virgin soils, the alkali occurs at considerable depths, and is mostly concentrated in a particular zone. Under the influence of irrigation, the salts rise to the surface. The best remedy would seem to be under-drainage, but, in the case of land of insufficient value, much can be done by careful surface flooding and suitable cropping.

N. H. J. M.

Distribution and Biological Importance of Furfuroids in Soil. By JULIUS STOKLASA (*Bied. Centr.*, 1899, 28, 588—589; from *Zeit. landw. Versuchswesen Oesterr.*, 1898, 1, 251—266. Compare Abstr., 1898, ii, 132).—The furfuroids in soil are produced by algæ and bacteria. The dry substance of *Pleurococcus vulgaris*, which grows on rocks, contains 3·43, that of *Nostoc*, 5·06 per cent. of pentosans. Cultures of *Bacillus mesentericus*, which is very common in soils, contained 2·31 per cent. of pentosans in the dry substance. *Parmelia*, *Lecanora*, *Hypnum Schreberi* and *H. dicranum*, and *Sphagnum cymbifolium* contain respectively 3·46, 3·43, 6·19, 10·78, and 15·44 per cent. of pentosans. Other plants of importance in peat production were found to contain the following amounts of pentosans: *Pteris aquilina*, 18·8; *Aspidium*, 19·1; *Equisetum arvense*, 33·5 and 21·1; *Lycopodium*, 24·6; *Carex acuta*, 19·6 in above-ground growth

and 26.5 in roots; *Calluna vulgaris*, 17.3 and 23.2 per cent. in above-ground growth and roots respectively.

Peat was found to contain 17.4 per cent. of pentosans in the first 10 cm., 10.38 per cent. at a depth of 50 cm., 5.34 per cent. at 100 cm., and 1.60 per cent. at a depth of 2 metres. The surface soil of forest land yielded 3.27, the soil at a depth of 50 cm. 0.83 per cent. of furfuraldehyde.

N. H. J. M.

Observations on the Growth of Maize continuously for Nine Years. By EDWARD H. JENKINS (*Ann. Rep. Conn. Agric. Exper. Stat.* for 1896, No. 20, 335—341).—The four plots received: (1) cow manure, (2) hog manure, (3) chemical manures, and (4) no manure. The average relative yield of dry produce from 1890—1896 was as follows: plot 1, 100; plot 2, 100.4; plot 3, 81.8; and plot 4, 51.0. Taking the produce of each plot as 100 in 1890, the following amounts were obtained in 1896. (1), 116; (2), 101; (3), 79; (4), 31.

The average composition (6 years) of the kernels and stalks was practically the same in the case of plots 1 and 2. In plot 3 (1,500 lbs. of chemical manure), the kernels contain rather less ash and fat, and 0.5 per cent. less proteids than those of plots 1 and 2, but more nitrogen-free extract. The stalks show similar differences. The kernels of the unmanured plot contain 2 per cent. less proteids, rather less ash and fat, but more fibre and nitrogen-free extract than those of plots 1 and 2.

The calculated gain or loss of manure constituents in the soil after 9 years cropping with maize was as follows in lbs. per acre:

Plot 1.			Plot 2.			Plot 3.			Plot 4.		
N	P ₂ O ₅	K ₂ O	N	P ₂ O ₅	K ₂ O	N	P ₂ O ₅	K ₂ O	N	P ₂ O ₅	K ₂ O
+1283	+893	+156	+2174	+3987	-7	+611	+1111	+171	-338	+46	-73

N. H. J. M.

Manurial Experiments with Barley. By JOSEPH HANAMANN (*Bied. Centr.*, 1899, 28, 638; from *Zeit. landw. Versuchswesen Oesterr.*, 1898, 1, 277—285).—The experiments were conducted in zinc vessels containing 12.5 kilograms of sandy soil, loamy sand, loam, and clay soil respectively (five pots in each case). One pot of each soil was without manure, whilst pots 2—4 received sodium nitrate and potassium chloride. The third pots had in addition superphosphate, the fourth pots basic slag (containing the same amount of phosphate as was given to No. 3), the fifth pots basic slag in double quantity.

The results indicate that spring manuring with basic slag is only advisable in the case of sandy soil, loamy sand, and peaty soil, but not in the case of loamy and clay soils, and the amount applied should be twice as great as that of superphosphate.

N. H. J. M.

Manurial Experiments with Lucerne. By MAX MAERCKER (*Bied. Centr.*, 1899, 28, 635; from *Landw. Jahrb.*, 1898, 27, 155).—It is thought that liberal application of phosphates will not only increase the yield of lucerne, but will be of use in preventing the injurious effects of lucerne on a succeeding cereal crop (liability to be laid, fungus attack, &c.).

N. H. J. M.

Experiments on the Availability of Fertiliser-Nitrogen. By SAMUEL W. JOHNSON, EDWARD H. JENKINS, and W. E. BRITTON (*Ann. Rep. Conn. Agric. Exper. Stat.* for 1896, No. 20, 178—204. Compare *ibid.*, No. 19, and Abstr., 1896, ii, 620).—The nitrogen availability of the different manures for maize grown in coal-ashes and peat, compared with that of sodium nitrate as 100, was found to be as follows (average of three years, 1894—6): collier castor pomace, 77; cotton seed meal, 74; red seal castor pomace, 70; linseed meal, 70; dried blood, 68; dry fish, 69; dissolved leather, 65; horn and hoof, 67; tankage, 61; steamed leather, 13; roasted leather, 9; raw leather, 2.

On comparing the nitrogen availability of some nitrogenous super-phosphates, determined by vegetation experiments, with the solubility in chemical agents, the following results were obtained:

	Available for maize.	Soluble in pepsin.	Soluble in permanganate. Acid.	Alkaline.
Blood	47	47	47	47
Tankage	45	39	45	43
Horn and hoof ...	43	28	42	52
Leather	3	8	14	25

The chemical methods would therefore seem to be of value as indicating the probable relative effect of inferior nitrogenous manures. The agricultural value cannot, however, at present be fixed without vegetation experiments.
N. H. J. M.

Manurial Experiment on Meadow Land. By MAX MAERCKER (*Bied. Centr.*, 1899, 28, 637; from *Landw. Jahrb.*, 1898, 27, 151).—The effect of potassium phosphate and of kainite was to increase the percentage of proteids in the hay owing, as a botanical separation of the herbage showed, to increased growth of more nitrogenous plants, especially *Leguminosæ*.
N. H. J. M.

Field Experiments on Peat Land, 1892—1897. By BRUNO TACKE (*Bied. Centr.*, 1899, 28, 589—611; from *Landw. Jahrb.*, 1898, 27, iv, 1—258. Compare Abstr., 1897, ii, 515).—Manure salts containing 38 per cent. of potash as potassium chloride gave very good results with potatoes, and had practically no injurious effect when applied in the spring in amounts of as much as 200 kilos. of potash per hectare. Carnallite and kainite (225 kilos.) applied in the spring considerably diminished both the yield of tubers and the amount of starch; in some cases there is a decrease of starch in the dry matter, in others the lower percentage of starch in the tubers is due to an increase in the amount of water. Application of lime seems to lessen the injurious effect of spring manuring with potash on potatoes.

Application of lime or marl to the soil for all kinds of crops is very beneficial for a time, and is even necessary when artificial manures are employed, but is subsequently injurious owing to the shrinking of the comparatively shallow layer of the surface soil. The injury can be overcome by subsoil liming.

Phosphoric acid in the form of phosphorite should only be applied to peat land which retains a certain degree of acidity.

N. H. J. M.

Manurial Experiments with Phosphorite and Basic Slag. By A. SEMPOLOWSKI (*Bied. Centr.*, 1899, 28, 637—638; from *Zeit. landw. Versuchswesen Oesterr.*, 1898, 1, 267—276).—Whilst hard crystalline phosphorite has to be converted into superphosphate, the so-called soft, non-crystalline mineral, if finely ground, can be employed, without further treatment, as manure. Experiments in which barley was grown in sandy loam and in peaty soil (contained in bottomless wooden boxes) manured with phosphorite meal and basic slag respectively, in addition to other manures, showed that the phosphorite was decidedly effective, the increased production of barley, over the unmanured plots being not much less than that obtained under the influence of basic slag. N. H. J. M.

Comparison between Bone- and Mineral-Superphosphate. By ANGELO MENOZZI (*Bied. Centr.*, 1899, 28, 635; from *Agricolt. moderna*, 1897, 50).—Maize grown in large zinc vessels was manured with equal amounts of phosphoric acid in the form of superphosphate from degelatinised bones and Florida phosphate respectively, in addition to other manures. The results indicated only slight superiority of the bone as compared with the mineral superphosphate. N. H. J. M.

Phosphate Deposits in Japan. By K. TSUNETO (*Chem. Zeit.*, 1899, 23, 800 and 825—827).—In 1894, large deposits of phosphates were discovered in the miocene formation, extending over 720 square kilometres, in the south-west of the island Kiushu. The phosphates occur in nodules and aggregates in the lime-sandstone, in marl veins, and in dark brown veins of sandstone situated between the calcareous fine-grained sandstone. The nodules are generally rich in phosphates in the inner portion, whilst the outer layer is rich in iron; they contain organic remains. The following is the percentage composition of (1) grey nodules, (2) light brown nodules, (3 and 4) aggregates, (5) balls, and (6) breccia:

	Water and organic.	K ₂ O.	Na ₂ O.	CaO.	MgO.	FeO.	Fe ₂ O ₃ .	Al ₂ O ₃ .	Mn ₂ O ₃ .	P ₂ O ₅ .	SO ₃ .	CO ₂ .	Insol.
1.	1.26	—	—	9.62	2.28	8.77	2.93	2.14	0.35	3.35	0.29	8.26	55.65
2.	1.48	—	—	12.71	2.28	8.95	2.99	2.88	0.39	4.76	0.53	7.08	55.25
3.	0.65	—	—	11.73	2.36	7.37	2.46	1.65	0.23	5.85	0.63	7.92	54.22
4.	0.89	—	—	10.56	1.14	7.88	1.64	2.00	—	7.14	0.51	6.81	57.43
5.	2.21	2.25	0.42	30.28	1.30	—	3.76	3.72	—	20.29	1.23	1.82	28.38
6.	2.15	1.04	0.42	16.76	1.20	—	3.89	1.98	—	9.47	trace	2.28	47.15

In (5), a trace of chlorine and 2.09 per cent. of fluorine were found, and in (6) Cl=0.06 and F=2.13 per cent.

Although the percentage of phosphoric acid is generally low, the deposits are of importance in Japan where manures with very low percentages of phosphates are utilised. The best method for utilising the minerals containing 5—10 per cent. of phosphates seems to be extraction of the ground substance with 12.45 per cent. sulphuric acid (avoiding too great a rise of temperature) in amounts sufficient to decompose the phosphates and carbonates present. N. H. J. M.

The Reversion of Soluble Phosphoric Acid in Superphosphates. By LUDWIG SCHUCHT (*Chem. Centr.*, 1899, i, 1165—1166; from *Chem. Ind.*, 22, 152—155).—Reversion does not take place unless the superphosphate is closely packed and consequently submitted to pressure. Ferric and aluminium compounds are harmful as their phosphates act on the undecomposed calcium triphosphate and so yield insoluble phosphates. Silicates are also a source of loss in phosphoric acid; their amount may be lessened by adding a regulated quantity of fluor-spar during the preparation of the superphosphate.

L. DE K.

Analytical Chemistry.

Standardising Acids. By ANTON SEYDA (*Chem. Centr.*, 1899, i, 1164; from *Zeit. öffentl. Chem.*, 5, 141—151).—Sodium carbonate, used for standardising acids, is likely to retain excess of carbon dioxide, or if overheated it may contain sodium hydroxide. A suitable article is, however, obtained by heating sodium hydrogen carbonate for an hour at 220° in an air-bath.

The results then perfectly agree with those obtained by standardising the acid with the aid of potassium hydrogen tartrate or ammonium chloride.

L. DE K.

Estimation of Sulphur in Bitumens. By STEPHEN F. PECKHAM and H. E. PECKHAM (*J. Amer. Chem. Soc.*, 1899, 21, 772—776).—In reply to Hodgson, the authors state that in order to get accurate estimations of sulphuric acid, any iron or aluminium oxides should be first removed.

The following method has been finally adopted for the estimation of sulphur in bitumen. A quantity of the substance representing about 0.5 gram of real bitumen is mixed with 15 grams of pure dry sodium carbonate and 15 grams of potassium nitrate and the mixture then fused by degrees in a platinum crucible. The product is dissolved in dilute hydrochloric acid, evaporated to dryness, and gently ignited to render any silica insoluble; the residue is then treated with dilute hydrochloric acid and the solution precipitated, while boiling, with a slight excess of ammonia to remove iron and aluminium. If desired, any calcium may be precipitated as oxalate. The filtrate is now acidified with hydrochloric acid and the boiling liquid precipitated with barium chloride solution added carefully from a pipette.

L. DE K.

Estimation of Hyposulphurous Acid. By N. FRADISS (*Chem. Centr.*, 1899, i, 1223; from *Bull. Assoc. Chimistes*, 16, 453).—The solution is neutralised and added from a burette to an ammoniacal standard solution of copper sulphate until this is quite decolorised. The presence of sulphites does not interfere. 1 mol. of hyposulphurous acid reduces 2 mols. of copper oxide to the cuprous state.

L. DE K.

Volumetric Estimation of Sulphuric Acid. By FRANZ LITTELSCHIED and KARL FEIST (*Arch. Pharm.*, 1899, 237, 521—525).—The authors have developed independently the method described by Grützner (this vol., ii, 530). The solution of the sulphate is acidified with hydrochloric acid, heated to boiling, treated with a measured excess of $N/4$ barium chloride solution, stirred well, and allowed to remain in a warm place for half-an-hour; the liquid is then made strongly alkaline with ammonia, excess of ammonium carbonate solution added, and the whole stirred and allowed to remain at 50—60° for ten minutes. The precipitate is then collected on a small filter, washed three or four times with hot water, and transferred to a conical flask, when the barium carbonate is titrated with $N/10$ hydrochloric acid. It may be titrated directly when methyl-orange is employed as an indicator; if phenolphthalein be used, excess of $N/10$ acid must be added, the carbon dioxide driven off by boiling, and the excess of acid titrated with $N/10$ caustic potash. On multiplying by 0.4 the number of c.c. of $N/10$ acid neutralised and subtracting the product from the number of c.c. of $N/4$ barium solution taken, the remainder multiplied by 0.01 gives the weight of SO_3 present, or multiplied by 0.004 the weight of S.

The solution of the sulphate must not contain any acid of which the barium salt is insoluble, such as phosphoric and oxalic acids; neither must it contain substances which are precipitated by ammonium carbonate, or, like tartaric and citric acids, hinder the precipitation of the barium. Alkaloids, if insoluble in ammoniacal ammonium carbonate solution, must be removed by extraction with a suitable solvent. The sulphates of potassium, sodium, ammonium, rubidium, cesium, copper, zinc, cadmium, nickel, and cobalt, may be estimated directly; so also that of lithium, provided the solution be dilute enough to retain the lithium carbonate in solution (solubility: 1 in 75 parts of water at 50°). Iron sulphate, and the solution obtained by oxidising copper pyrites with nitric acid and potassium chlorate, may also be estimated, if the iron is first removed as hydroxide. With magnesium sulphate, good results have not yet been obtained. C. F. B.

Titration of Persulphates. By MAX LE BLANC and M. ECKARDT (*Zeit. Elektrochem.*, 1899, 5, 355—357).—The reaction between a persulphate and a ferrous salt in solution is comparatively slow at the ordinary temperature; erroneous results may therefore be obtained in the analysis of persulphates by treating the solution with ferrous sulphate and titrating the excess with permanganate. These errors are very easily avoided by warming the acidified mixture of persulphate and ferrous ammonium sulphate to 60—80° before titrating with permanganate T. E.

Estimation of Tellurous Acid in Presence of Haloid Salts. By FRANK A. GOOCH and C. A. PETERS (*Amer. J. Sci.*, 1899, 8, 122—126).—Tellurous acid is generally estimated by adding to its alkaline solution a slight excess of standard potassium permanganate. A definite volume of standardised ammonium oxalate is added, and then a sufficiency of dilute sulphuric acid (1:1) so as to have about 5 c.c. of the acid in excess. After heating at 60—80°, the excess of oxalic acid is estimated by standard permanganate.

The authors find that the presence of chlorides does not interfere if before the final titration about 1 gram of crystallised manganous chloride is added. Bromides are also harmless if the same precaution is taken and the temperature not allowed to rise above 25°.

In the case of iodides, the process breaks down, so another method was successfully tried. The alkaline solution is mixed with a known volume of potassium permanganate, previously standardised with a standard solution of arsenious acid, and, after a while, a slight excess of dilute sulphuric acid is added, with, if necessary, some more potassium iodide; after adding a slight excess of potassium hydrogen carbonate, the liberated iodine is titrated with the standard solution of arsenious acid, the end reaction being the disappearance of the yellow colour; starch need not be used as an indicator.

Supposing the two solutions balance each other—the difference in the two titrations equals the number of c.c. of permanganate consumed by the tellurous acid.

L. DE K.

Detection of Nitric Acid in Cadaveric Matter. By DIOSCORIDE VITALI (*Zeit. anal. Chem.*, 1899, **38**, 539—541; from *Oesterr. Chemikerzeit.*, **1**, 330).—For the detection of free nitric acid in animal matter in which nitrates may already be present, either as normal constituents or by introduction in food, it is useless to distil with water, for the mineral acids combine with albumin, forming acid-albumins, which in many cases are not decomposed at 190°. The substance is therefore digested on the water-bath with freshly precipitated barium carbonate, the solution evaporated to dryness, and the residue boiled repeatedly with absolute alcohol for the removal of calcium and magnesium nitrates. The alcoholic solution will also contain the soluble acid-albumin. It is evaporated to dryness, the residue dissolved in water, and exactly neutralised with barium hydroxide solution, which decomposes the acid-albumin. The solution is again evaporated and the nitrates separated by absolute alcohol. The residual barium nitrate is then dissolved in water, decolorised with lead acetate, freed from lead by hydrogen sulphide, and the concentrated solution finally crystallised in the desiccator. The residue from the first treatment with alcohol contains the barium nitrate derived from the presence of free acid as well as insoluble acid-albumin, and possibly some calcium nitrate. It is treated with a dilute solution of sodium carbonate until an alkaline reaction is just obtained. The acid-albumin and the barium nitrate are by this means converted into sodium nitrate, the calcium nitrate remaining undecomposed. The filtered solution is evaporated to dryness and the residue boiled with absolute alcohol. The sodium nitrate dissolves, but it is stated that the calcium nitrate remains undissolved. The sodium nitrate is purified and identified in the same way as the barium nitrate above. [W. Fresenius expresses grave doubts as to the correctness of some of the above reactions, and points out that the author contradicts himself, as well as established fact, in stating that calcium nitrate is undissolved by boiling alcohol.]

Another method consists in treating the animal matter with freshly precipitated strychnine, when strychnine nitrate is formed. This

can be purified by solution in boiling alcohol, the colour removed with lead acetate, and the nitrate finally obtained as crystals.

A very sensitive reaction for nitric acid is obtained by adding salicin and 8—10 drops of concentrated sulphuric acid to the residue of an evaporated solution. A blood-red coloration is produced, which becomes violet on dilution.

M. J. S.

Estimation of Arsenic in Paris Green. By THORN SMITH (*J. Amer. Chem. Soc.*, 1899, 21, 769—772).—Two grams of the sample are boiled with 100 c.c. of water and 2 grams of sodium hydroxide; when cold, the liquid is made up to 250 c.c., well shaken, and filtered through a dry filter. 50 c.c. are then concentrated to 25 c.c., and after cooling to 80°, 25 c.c. of hydrochloric acid and 3 grams of potassium iodide are added. After remaining for 10 minutes, any arsenic acid will be completely reduced to the arsenious state and the liberated iodine is removed by diluting with water and carefully decolorising with solution of sodium thiosulphate. After first neutralising with, and then adding an excess of sodium hydrogen carbonate, the arsenious acid is titrated in the usual manner with $N/10$ solution of iodine.

L. DE K.

Estimation of Boric Acid in Tourmaline. By GEORGE W. SARGENT (*J. Amer. Chem. Soc.*, 1899, 21, 858—887).—The paper contains a summary of all the chief methods proposed for the estimation of boric acid, and the author's opinion as to their respective merits.

When dealing with tourmaline and similar minerals containing aluminium, the chief difficulty arises from the incomplete separation of boric acid and alumina, the only way of effecting complete separation is by the method proposed by Gooch, namely, volatilisation of the acid by means of methyl alcohol, coupled with the titration of the volatilised acid by Thomson's glycerol method.

L. DE K.

Iodometric Method for the Estimation of Boric Acid. By LOUIS C. JONES (*Amer. J. Sci.*, 1899, 8, 127—132. Compare Abstr., 1899, ii, 332).—Under certain definite conditions, a mixture of boric acid and mannitol possesses an acidic power sufficiently strong to liberate iodine from a mixture of potassium iodide and iodate. The iodine is readily estimated by means of sodium thiosulphate, and represents the amount of boric acid.

To obtain correct results, the following mode of procedure should be used: the borate is dissolved in the smallest possible quantity of hydrochloric acid and then diluted with water so that 50 c.c. of liquid shall contain about 0.1 gram of boric acid. The greater part of the free acid is then neutralised with sodium hydroxide and 5 c.c. of a 40 per cent. solution of potassium iodide and 10 c.c. of a 5 per cent. solution of potassium iodate are added and the liberated iodine at once removed by a few drops of a strong solution of sodium thiosulphate. After restoring a very faint yellow colour by means of standard iodine, 15 grams of mannitol are added, and when dissolved, a standard solution of sodium thiosulphate is added until the colour is bleached, when an extra 10 c.c. are added. A little more mannitol is added and after standing in a cool place for an hour, the excess of thiosulphate is carefully titrated by means of standard iodine solution.

L. DE K.

Stutzer and Hartleb's Process for the Estimation of Combined Carbon Dioxide (Calcium Carbonate) in Soils. By H. SCHÜTTE (*Zeit. angew. Chem.*, 1899, 854—858).—The author criticises this process (*Abstr.*, 1899, ii, 521) and states that, although good enough for marls, it is not sufficiently accurate for the estimation of small quantities of calcium carbonate in soils.

The chief objection to the process is that ammonium chloride also acts on calcium in combination with silicic acid, and so causes the results to be in excess of the truth. Ferrous carbonate is also stated to interfere with the accuracy of the method, and cannot always be completely decomposed by boiling.

L. DE K.

Gas Washing Apparatus: Rapid and Accurate Process for the Estimation of Carbon Dioxide. By ROBERT SCHALLER (*Zeit. angew. Chem.*, 1899, 878—880).—The apparatus is essentially a U-tube 17 cm. long, one side of which is very narrow and serves to admit the current of the gas. The other side is filled with glass beads 2 mm. in diameter, which are moistened with the absorbing liquid.

In the new apparatus for estimating carbon dioxide, the substance is decomposed in a kind of test-tube with hydrochloric acid, and the carbon dioxide is swept out by means of a current of air which has been freed from this gas by passing through two of the U-tubes containing a solution of potash. The gas then passes through a similar tube containing sulphuric acid before it reaches the absorber. The latter consists of one or two similar weighed U-tubes containing 10 c.c. of 50 per cent. solution of potassium hydroxide. These tubes are, in addition, fitted with a small test-tube 8 cm. long containing 1 c.c. of strong sulphuric acid, and provided with a doubly perforated rubber cork. Through one of the holes passes a tube with a bulb in its centre and drawn to a narrow point at the bottom, the object being to prevent any escape of moisture from the apparatus. The other hole is fitted with a small bent tube to allow the air to escape.

L. DE K.

Estimation of Calcium Carbonate in Marls. By HERMANN NOLL (*Zeit. angew. Chem.*, 1899, 859—860).—The process recommended by Tacke is found to answer for the estimation of calcium carbonate in marls, as it is not affected by the presence of small quantities of ferrous and aluminium compounds or of calcium silicate. The details of this process are briefly as follows: 0.2 gram of the powdered sample is mixed with 200 c.c. of warm water, 25 or 50 c.c. of $N/5$ normal sulphuric acid are added, and the carbon dioxide expelled by boiling. The excess of acid is then titrated with standard baryta, using phenolphthalein as indicator.

L. DE K.

New Volumetric Method for the Estimation of Magnesium. By RICHARD K. MEADE (*J. Amer. Chem. Soc.*, 1899, 21, 746—752).—The process is an indirect one. The ammoniacal solution free from calcium is precipitated with a solution of sodium arsenate, and the excess of the reagent removed by washing with dilute aqueous ammonia (1:3). The arsenical precipitate is then dissolved in 75—100 c.c. of dilute

hydrochloric acid (1:1), potassium iodide added, and the liberated iodine titrated with standard solution of sodium thiosulphate.

L. DE K.

Double Ammonium Phosphates of Beryllium, Zinc, and Cadmium in Analysis. By MARTHA AUSTIN (*Amer. J. Sci.*, 1899, 8, 206—216).—When salts of these three metals are precipitated by boiling with excess of sodium ammonium hydrogen phosphate, double ammonium phosphates are obtained, which, on ignition, yield the corresponding pyrophosphates.

It has, however, been found impossible to accurately estimate beryllium in this manner. Zinc may be estimated if care be taken to precipitate the metal from a neutral solution containing 10 per cent. of ammonium chloride. The process is also well adapted for cadmium; the solution should contain 10 per cent. of ammonium chloride, be practically neutral, and be allowed to remain several hours before filtering.

L. DE K.

Analysis of Zinc for Cadmium and Lead. By P. A. MACKAY (*J. Amer. Chem. Soc.*, 1899, 21, 940—941).—The metal is treated with dilute hydrochloric acid in sufficient quantity to dissolve the bulk of the zinc; the undissolved portion then contains all the lead and cadmium present.

After dissolving the residue in nitric acid, the lead is recovered in the usual way as sulphate, and in the filtrate the cadmium is precipitated by hydrogen sulphide; the cadmium sulphide is then collected, washed, and redissolved in boiling hydrochloric acid and titrated with potassium ferrocyanide. It has been noticed, however, that small quantities of cadmium can only be accurately estimated in the presence of zinc, and also that 1 gram-mol. of cadmium requires 3·676 gram-mols. of potassium ferrocyanide, instead of 3·767, as required by theory. A solution containing 10 grams of zinc per litre is prepared, and 50 c.c. of this titrated with a solution containing 36·76 grams of potassium ferrocyanide per litre, using uranium acetate as indicator. Another 50 c.c. is then added to the liquid containing the cadmium, and the titration is repeated; each c.c. excess of ferrocyanide solution used in this titration represents 0·01 gram of cadmium.

L. DE K.

Electrolytic Estimation of Zinc in the Presence of Manganese. By EMIL J. RIEDERER (*J. Amer. Chem. Soc.*, 1899, 21, 789—792).—Zinc may be conveniently separated from manganese by electrolysis. The solution, which should not contain chlorides or nitrates, but only sulphates, is mixed with 5 grams of ammonium lactate, 0·75 gram of lactic acid, 2 grams of ammonium sulphate, and then made up to 230 c.c.; the amount of zinc should not exceed 0·17 gram. The cathode, which should be 1½ cm. distant from the anode, should consist of a platinum dish on which silver has been deposited, and during the action of the current it is advisable to use a mechanical stirrer so as to obtain an even and uniform deposit of zinc; the current may vary from 0·20—0·26 ampères and the temperature from 15—26°.

The time required for the complete deposition of the zinc does not

exceed $5\frac{1}{2}$ hours; the deposit is free from manganese. It is rapidly washed first with water, then successively with alcohol and ether, dried in the water oven for 5 minutes, and weighed. L. DE K.

Direct Estimation of Aluminium in the Presence of Iron, Manganese, Calcium, and Magnesium. By WILLIAM H. HESS and EDWARD D. CAMPBELL (*J. Amer. Chem. Soc.*, 1899, 21, 776—780).—A convenient bulk of the liquid, preferably containing the metals as chlorides, is heated to boiling and dilute ammonia is added so long as the precipitate readily redissolves; to reduce the ferric salts, a saturated solution of ammonium hydrogen sulphite is added drop by drop until the liquid is colourless. The aluminium is now precipitated by adding a few c.c. of phenylhydrazine and is washed with hot water containing about 10 per cent. of phenylhydrazine hydrogen sulphite free from excess of sulphur dioxide. On ignition, it leaves pure alumina. Chromium may also be separated from iron, calcium, magnesium, cobalt, or nickel in this manner.

If, however, the mixture also contains phosphoric acid, the alumina will be contaminated with phosphoric oxide, which must be estimated and allowed for. L. DE K.

Volumetric Estimation of Manganese. By RODOLFO NAMIAS (*Chem. Centr.*, 1899, i, 1224; from *Annuar. Soc. chim. Milano*, 1899, 54—56).—The author uses Volhard's process when estimating manganese in samples of iron or steel. Use is made of carefully selected crystals of potassium permanganate which are reduced by boiling with hydrochloric acid; the manganous chloride so obtained is precipitated with sodium carbonate, the precipitate is converted into manganoso-manganic oxide, and this is titrated with ferrous sulphate.

It is recommended to first dissolve the steel, or iron, in hydrochloric acid before oxidising with nitric acid to prevent the formation of organic compounds, which reduce permanganate. L. DE K.

A Simplified Reductor. By PORTER W. SHIMER (*J. Amer. Chem. Soc.*, 1899, 21, 723—724).—A new form of the reductor used in the estimation of iron and phosphomolybdate solutions. It is essentially a plain glass tube $\frac{3}{8}$ -inch in diameter and 20 inches long drawn out and cut off at the lower end. It is united with a 4-inch funnel by means of wired rubber tubing fitted with a screw clamp. The lower end passes through a soft two-hole stopper of a thick-walled pint gas bottle connected with a filter pump through an intermediate safety bottle and valve. The passage of the solution through the reductor may be effected either by use of the pump or by Bunsen's device of condensing steam.

The tube is filled by placing a few small pieces of broken glass in the drawn out portion, then a little clean sand and finally about 3 ounces of amalgamated zinc. The speed of filtration is regulated by the upper clamp; a reduction takes about five minutes.

L. DE K.

Separation of Iron from Chromium, Zirconium, and Beryllium by the Action of Hydrogen Chloride on the Oxides. By FRANK S. HAVENS and ARTHUR F. WAY (*Am. J. Sci.*, 1899, 8, 217—218).—Gooch and Havens (*Abstr.*, 1897, ii, 232) have shown that iron

oxide may be readily separated from alumina by heating the mixed oxides in a current of hydrogen chloride at a temperature of 450—500°; if to the mixture of sodium chloride and sulphuric acid a small quantity of manganese dioxide is added so as to also generate a little chlorine, the decomposition may be effected at 200—300°.

The authors now state that this method may be used successfully for the separation of oxide of iron from the oxides of chromium, zirconium, and beryllium.

L. DE K.

Estimation of Nickel in Nickel-steel. By GEORGE W. SARGENT (*J. Amer. Chem. Soc.*, 1899, 21, 854—857).—The metal is dissolved in hydrochloric acid, oxidised with nitric acid, and the solution evaporated to dryness; the residue is taken up with a little dilute hydrochloric acid, and filtered into a separating funnel. The bulk of the ferric chloride is now removed by agitating the liquid with ether (Chase's method) and the solution, after removal of the dissolved ether, precipitated by bromine water and ammonia; the precipitate is freed from nickel by a second solution and precipitation. The combined filtrates containing the nickel are acidified with hydrochloric acid, freed from any copper by hydrogen sulphide, the filtrate boiled to expel hydrogen sulphide, and, when cold, a slight excess of ammonia added, and the liquid titrated with standard potassium cyanide, with silver iodide emulsion as indicator (Campbell and Andrew's method, *Abstr.*, 1895, ii, 421).

L. DE K.

[**Estimation of Chromic Acid in Acetylene Purifiers.**] By FRITZ ULLMANN and IRMA GOLDBERG (*Chem. Centr.*, 1899, ii, 19—20; from *J. Gasbel.*, 42, 374—377).—See this vol., i, 1.

Estimation of Antimony in Ores. By THOMAS BROWN, jun. (*J. Amer. Chem. Soc.*, 1899, 21, 780—789).—*Assay of soluble ores such as Stibnite and Senarmontite.*—1 gram of the finely powdered sample is boiled in a covered beaker with 25 c.c. of strong hydrochloric acid until about 15 c.c. are left. 2 grams of tartaric acid are then added, and when dissolved, about 4—6 drops of strong nitric acid are introduced, and the boiling continued for a minute. The mixture is then diluted with water, the insoluble residue well washed on a filter, and the filtrate diluted to about 250 c.c. The liquid is now saturated with hydrogen sulphide and gently heated, and after remaining for an hour, the antimony sulphide is collected and washed with cold water. If there is any probability of lead being present, the precipitate must be dissolved in ammonium sulphide and the filtrate reprecipitated with dilute hydrochloric acid. The precipitate is collected on a counterpoised (double) filter, washed, dried at 110°, and weighed; the bulk of the crude antimony sulphide is transferred to a weighed platinum boat, and then placed inside a piece of combustion tube and heated in a current of carbon dioxide, so as to convert it into black antimony sulphide, which is then weighed. A correction is finally made for the small amount of sulphide not removable from the filter.

Assay of insoluble ores such as Cervantite.—1 gram of the powdered ore is mixed in a covered porcelain crucible with 10 grams of a mixture of equal parts of sulphur and dry sodium carbonate, covered with a little more of this flux, and fused for 10 minutes in a muffle. The mass

is extracted with water, and in the filtrate the antimony is precipitated as sulphide by means of hydrochloric acid; the crude sulphide is then treated as previously directed.

Assay of partially soluble ores: Oxysulphides.—These are assayed by the combination of the two processes described.

The fire assay (fusion with potassium cyanide), although easy of execution, seldom agrees with the wet assays, and is particularly unsuitable for ores containing sulphur. L. DE K.

Apparatus for the Preparation of Plant-Ash for Analysis. By G. M. TUCKER (*Ber.*, 1899, 32, 2583—2585).—This is a simplified form of Shuttleworth's apparatus (*Diss. Göttingen*, 1899, and *J. Landwirtschaft*, 1899, 173) designed to give a control over any loss of potash, chlorine, &c., by volatilisation. The platinum vessel, in which the plant is burnt, is of a conical form and is provided with a closely-fitting cover having two apertures. In the central aperture is soldered a tube passing to the bottom of the vessel and down this tube, by means of which air enters, passes the handle of a stirrer. By means of the other aperture, the gases from the combustion chamber are led through a small wash-bottle, beyond which is an aspirator which draws air through the whole apparatus. Any ash mechanically carried by the air stream is stopped by a loose movable cap fitted to the exit tube. The conical shape of the vessel allows of more uniform heating, which is carried out first in a conical sand-bath, and, later, over a bare flame, the vessel being then fitted into a hole in an asbestos card. T. H. P.

Ammoniacal Copper Solutions and Hydroxylamine as a Test for Acetylene. By LUDWIG ILOSVAY VON NAGY ILOVA (*Ber.*, 1899, 32, 2697—2699).—Ammoniacal copper solutions decolorised by reducing with hydroxylamine can be used for detecting acetylene, but the value of the reagent and the colour of the precipitate depend on the proportions used. The quantities recommended are, for 50 c.c. of solution, (I) cupric chloride ($+ 3\text{H}_2\text{O}$), 0.75 gram; ammonium chloride, 1.5 grams; aqueous ammonia (20—21 per cent.), 3 c.c., hydroxylamine hydrochloride, 3 grams. (II) cupric nitrate ($+ 5\text{H}_2\text{O}$), 1 gram; aqueous ammonia, 4 c.c., hydroxylamine hydrochloride, 3 grams. (III) copper sulphate ($+ 5\text{H}_2\text{O}$), 1 gram; aqueous ammonia, 4 c.c., hydroxylamine hydrochloride, 3 grams. The reagent gives a splendid red precipitate with acetylene, but begins to deteriorate after three days. T. M. L.

A Colour Test for the Detection of Methyl Alcohol. By EDMOND JANDRIER (*Chem. Centr.*, 1899, i, 1296; from *Ann. chim. anal. appl.*, 4, 156).—Resorcinol recommended by Mulliken and Scudder (*Abstr.*, 1899, ii, 388) gives, with acetaldehyde, almost the same colour as with formaldehyde, and is consequently not a safe test for the detection of methyl alcohol; the test is also interfered with by the presence of furfuraldehyde. It is proposed to use gallic acid instead, as recommended by Barbet and Jandrier (*Abstr.*, 1898, ii, 265). L. DE K.

Recognition of Marc Wines (Tresterweine). By WILHELM FRESSENIUS and LEO GRÜNHUT (*Zeit. anal. Chem.*, 1899, 38, 472—512).—Wines obtained by the fermentation of solutions of glucose in

contact with grape marc (*Trester*) have hitherto not been distinguishable with certainty by chemical analysis from natural wines. The authors believe they have discovered a trustworthy criterion of such wines in the fact that they contain little or no tartaric acid combined with alkaline earths, whilst natural white wines always contain calcium tartrate to an extent which permits a limit of about 0.1 gram of tartaric acid per 100 c.c. to be established. The recognition of this fact in their composition depends on the estimation of the ratio of the total tartaric acid to the total alkalinity of the ash and the alkalinity of the portion of the ash soluble in water. With reference to the observations of Kulisch, Kohlmann, and Höppner (*Abstr.*, 1899, ii, 341; also 1895, ii, 465) on this subject, they point out that, in the estimation of the soluble constituents of the ash, a very limited amount of washing (30—80 c.c. of hot water for the ash of 100 c.c. of wine) must be employed, so as to leave the calcium carbonate of the ash as far as possible undissolved. Formulæ are given for calculating the analytical data. An exception to the above rule occurs in the case of marc wines to which tartaric acid has been added during manufacture. Red wines also contain much smaller proportions of calcium tartrate than white wines. The above criterion must therefore in all cases be considered in connection with other characteristics of marc wines, namely, a high proportion of ash to total solids, high percentage of tannin, and occasionally also of volatile acids. It can likewise only be employed in cases where the ash of the wine exhibits a normal total alkalinity and the proportion of sulphate is not abnormal, since it is obvious that excessive sulphuring would disturb the relations of the various tartrates in the wine. The alkalinity factor of natural wines, that is, the alkalinity of 0.1 gram of the ash expressed in cubic centimetres of normal alkali, seldom exceeds 0.8 or 1.0. Wines exhibiting a much lower alkalinity factor should be examined for excessive sulphuration. A much higher factor would suggest a search for added organic acids. The ratio of glycerol to alcohol in marc wines seems generally to exceed the limit of 7:100 laid down for natural wines.

With regard to the use of the large proportion of tannin as a criterion of marc wines, it is evident that no limit can be laid down, since the proportion of tannin in natural wines varies widely. Barth has argued that the ratio of total extract (after deduction of sugar, ash, and non-volatile acids) to tannin may be regarded as constant, and employs the factor 5 for multiplying the tannin. The authors show, however, that in a great number of natural wines, even the factor 4 would be too high and point out the need for further investigations of this subject.

The authors also give a complete analysis of the ash of a marc wine prepared by themselves, and some analyses of raisin-wines, one of which they also manufactured.

M. J. S.

Volumetric Estimation of Alcohols, especially of Fusel-Oil in "Brandies." By FRANZ ADAM (*Chem. Centr.*, 1899, i, 1226—1227; from *Oesterr. Chem. Zeit.*, 2, 241—243).—A solution of acetyl chloride in chloroform, after it has been well shaken with water and so

decomposed into acetic and hydrochloric acids, is titrated with normal alkali. Another portion of the chloroform solution is allowed to act on the alcohol, whereby it is partly decomposed into hydrogen chloride and alkyl acetate; after decomposing the remainder with water, the titration is repeated, and the difference in alkali represents the amount of the alcohol. To estimate amyl alcohol in brandy, the sample is diluted to 20 per cent. strength by volume, and the fusel oil then extracted by repeated agitation with pure chloroform. This is repeatedly shaken with water, then dried over burnt gypsum and treated with standard solution of acetyl chloride, &c. The process is also suitable for the estimation of the alcohol number of ethereal oils.

L. DE K.

Action of Bromine on Phenol and Cresols with Reference to the Analysis of Mixtures of these Compounds. By HUGO DITZ and FRANZ CEDIVODA (*Zeit. angew. Chem.*, 1899, 873—877 and 897—903).—An alkaline solution of a phenol is mixed with a known excess of bromine dissolved in caustic potash, acidified with dilute HCl (1:1), shaken vigorously for 1 minute, and titrated with standard thiosulphate solution in the presence of potassium iodide; under these conditions, 1 mol. of *o*-cresol or *p*-cresol takes up 2 atoms of bromine, whilst *m*-cresol and phenol each combine with 3 atoms. In the case of *p*-cresol, it is essential that the duration of the experiment should not exceed the prescribed time limit, otherwise the amount of bromine required exceeds 2 atoms. When the alkaline solution of a phenol and excess of bromine is acidified with concentrated sulphuric acid, allowed to remain for 10 minutes, subsequently shaken for 5 minutes, and then filtered through glass wool or sand, it is found, by treating the filtrate with potassium iodide and titrating with thiosulphate, that the amount of bromine taken up corresponds with 3 atoms in the case of *o*-cresol and *p*-cresol, and with 4 for *m*-cresol and phenol. These results are applied to the analysis of mixtures of two or more of these constituents. The mixture of the phenols is separated from other impurities by extraction with ether; the ethereal extract is dried over calcium chloride or dry sodium sulphate, distilled up to 180° to remove ether and last traces of moisture, the fraction distilling over above this temperature is treated with bromine by the two methods just described, and the amount of phenol, *m*-cresol and mixed ortho- and para-cresol determined by means of the following equations: (i) $x + y + z = a$; (ii) $3\text{Br}/94.06.x + 2\text{Br}/108.08.y + 3\text{Br}/108.08.z = b$; and (iii) $4\text{Br}/94.06.x + 3\text{Br}/108.08.y + 4\text{Br}/108.08.z = c$, where x and z represent the amounts of phenol and *m*-cresol, y the amount of the mixture of the ortho- and para-isomerides, a the total quantity of phenolic compounds, b the amount of bromine absorbed when the solution is acidified with dilute hydrochloric acid, and c the amount taken up when concentrated sulphuric acid is employed, and the bromo-derivatives filtered off before titration.

G. T. M.

Simplification of the Phenylhydrazine Test [for Sugar in Urine.] By ALBERT KOWARSKY (*Chem. Centr.*, 1899, i, 1294; from *Berl. klin. Wochschr.*, 36, 412—414).—5 drops of pure phenyl-

hydrazine are mixed with 10 drops of glacial acetic acid and 1 c.c. of brine, and the mixture boiled for 2 minutes with 3 c.c. of the supposed diabetic urine and then allowed to cool slowly. If the characteristic osazone crystals form after a few minutes, the urine is practically free from sugar. If appreciable traces of albumin are present, these must be first removed by coagulation at the boiling heat.

L. DE K.

Stability of Gun-Cotton and Smokeless Powder. By C. HOITSEMA (*Zeit. angew. Chem.*, 1899, 705—710).—A review of the methods in use for testing these explosives as to their keeping powers.

The author thinks that at present there are not sufficient grounds for substituting the Simon-Thomas test for those of Abel and of Guttman. For comparison, a stock of materials of guaranteed make and of known age should be kept.

L. DE K.

Chemistry of Butter-Fat. II. Chemical Composition of Butter-Fat. By C. A. BROWNE, jun. (*J. Amer. Chem. Soc.*, 1899, 21, 807—827. Compare Abstr., 1899, ii, 709).—This is a long investigation as to the true composition of butter-fat; on the whole, the article does not lend itself to useful abstraction.

The following analysis of the fatty acids obtained from 100 grams of butter is interesting as it confirms the result of Hehner and Mitchell (Abstr., 1897, ii, 287) as to the small proportion of stearic acid contained in butter: dihydroxystearic, 1.00; oleic, 32.50; stearic, 1.83; palmitic, 38.61; myristic, 9.89; lauric, 2.57; capric (decoic), 0.32; caprylic (octoic), 0.49; caproic (hexoic), 2.09; butyric acid, 5.45; total, 94.75.

L. DE K.

The Reichert Number of Butter. By JAMES H. STEBBINS (*J. Amer. Chem. Soc.*, 1899, 21, 938—940).—From the result of 317 analyses of genuine butters, the author is in favour of placing the lowest allowable limit of the Reichert number at 11.5.

L. DE K.

Analysis of Bees Wax. By ANGIOLO FUNARO (*L'Orosi*, 1899, 22, 109—123).—The adulterants of bees wax are Japan and Carnauba wax, animal fats, stearic acid, resins, cerasin, and paraffin wax. The various methods for detecting and estimating these impurities are described in detail and discussed.

T. H. P.

The Sesamé Oil Reaction and Sesamé Butter. By KARL BERNHARD SOHN (*Bied. Centr.*, 1899, 28, 298—299; from *Milchzeit.*, 1898, 498).—The employment of pure furfuraldehyde which has been recently distilled in a vacuum, and is colourless, is of great importance in testing for margarine by means of the Baudouin test. In case pure furfuraldehyde is not available, the employment of furfuramide is recommended.

The following process for detecting for sesamé oil is given: the melted filtered butter (10 c.c.) is extracted with hydrochloric acid of sp. gr. 1.125 three or four times or until the acid remains colourless. Five c.c. of the butter fat is then shaken with a solution of 1.08 grams of furfuramide in 100 c.c. of absolute alcohol (0.1 c.c.) and hydrochloric acid of sp. gr. 1.19 (10 c.c.) for at least half a minute. If the fat solidifies, it is heated at 60—70°. If the hydrochloric acid

shows a red coloration which does not soon disappear, sesame oil is proved to be present; with small amounts of sesamé oil, the coloration takes hours to appear. N. H. J. M.

[Testing Butter for Oil of Sesamé.] By H. WEIGMANN (*Bied. Centr.*, 1899, 28, 629).—See this vol., ii, 40.

Detection and Estimation of Formaldehyde in the Free State and in its Compounds. By G. H. A. CLOWES and BERNHARD TOLLENS (*Ber.*, 1899, 32, 2841—2848).—Formaldehyde is estimated by heating with phloroglucinol and hydrochloric acid at 70—80° and weighing the phloroglucide, $C_7H_6O_3$, which is produced under these conditions. In most of its compounds, the formaldehyde can be estimated in this way by using hydrochloric acid and water, but in some cases it is necessary to employ a more or less concentrated sulphuric acid to hydrolyse the methylene compound. A large number of analytical results are given. T. M. L.

[Separation of Acetone from Acetoacetic and Acetonedi-carboxylic Acids]. By LUIGI SABBATANI (*Chem. Centr.*, 1899, ii, 22—23; from *Atti Real. Accad. Torino*, 34).—See this vol., ii, 32.

New Reaction of Acetone and a New Method for the Detection of Aliphatic Amines. By ENRICO RIMINI (*L'Orosi*, 1899, 22, 40—44).—If to a mixture of an aliphatic monamine with a 10 per cent solution of acetone a few drops of a concentrated solution of sodium nitroprusside are added, a magenta coloration is formed, which gradually becomes more and more intense and lasts for several hours; the addition of a few drops of acetic acid changes it to an intense violet. When the hydrochloride of the amine is employed, too much alkali must not be added, as in this case the orange tint of Legal's reaction is obtained; this, however, vanishes much more quickly than the red coloration. By using aniline or phenylhydrazine in place of the aliphatic monamine, no coloration is obtained, whilst benzylamine gives a faint violet colour which forms slowly. With secondary aliphatic monamines, Legal's reaction takes place, whilst tertiary amines act simply as alkalis.

No coloration is obtained if, instead of acetone, one of the following substances is employed:—formaldedyde, acetaldehyde, paraldehyde, isobutaldehyde, or valeraldehyde, chloral, benzaldehyde, salicylaldehyde, anisaldehyde or cinnamaldehyde, furfuraldehyde, dextrose, acetophenone, benzophenone, ethyl acetoacetate, camphor, fenchone, or tanacetone; with concentrated solutions of pyruvic acid, a brown coloration forms and changes to green, whilst with dilute solutions a ponceau tint is developed.

The presence of 1/10 per cent. of acetone in a solution can be detected in this way, and the formation of the colour is not interfered with by the presence of alcohol or acetaldehyde.

Use is made of this reaction of acetone and of that of acetaldehyde formerly described (*Rendiconti Amministr. Civile. Ministero del Interno*, 1898) by the author to distinguish between primary and secondary aliphatic amines. The formation of an azure coloration on adding sodium nitroprusside and aldehyde to the solution of an amine, shows

that the base is secondary, whilst if acetone is added in place of the aldehyde, and a magenta tint is given to the liquid, the amine is primary. These reactions are obtained in mixtures of primary, secondary, and tertiary amines.

T. H. P.

Volumetric Estimation of Quinones Derived from Benzene. By AMAND VALEUR (*Compt. rend.*, 1899, 129, 552—553).—The method described is based on the reduction of quinones by hydriodic acid, all secondary reactions being avoided by operating in the following manner. A cooled mixture of 20 c.c. of concentrated hydrochloric acid with an equal volume of 95 per cent. alcohol is quickly added to 20 c.c. of a 10 per cent. aqueous solution of potassium iodide. The liquid is then poured into the alcoholic solution of the quinone and the iodine liberated is titrated with $N/10$ sodium thiosulphate solution. The process is expeditious, and is shown to give accurate results in the case of quinone, dichloroquinone, toluquinone, and thymoquinone; it is also applicable to unstable compounds of quinones, such as phenoquinones and quinhydrones.

N. L.

A Colour Reaction to Distinguish the Hydrochlorides of *m*-Phenylenediamine and *p*-Phenylenediamine. By L. CUNIASSE (*Chem. Centr.*, 1899, i, 1297; from *Ann. chim. anal. appl.*, 4, 156—157).—The meta-compound, when heated in aqueous solution with a few drops of a 1 per cent. solution of acetaldehyde in proof-spirit slightly acidified with acetic acid, yields, when cold, a splendid yellow coloration with a strongly green fluorescence. The para-compound turns orange-red without any fluorescence.

L. DE K.

Estimation of Urea in the Tissues: and the Amount contained in the Liver. By RUDOLF GOTTLIEB (*Chem. Centr.*, 1899, i, 1298; from *Arch. Exp. Path. Pharm.*, 42, 238—249).—The urea is first isolated as a mercuric compound by von Schroeder's process; finally, the alcoholic solution of the urea is precipitated by an ethereal solution of oxalic acid and the acid contained in the urea oxalate found by titration.

The blood of starving dogs contains 0.011—0.02 per cent. of urea; when on meat diet, it increases to 0.033—0.056 per cent. The liver, contrary to expectation, contains only 0.008—0.02 per cent.

L. DE K.

Detection of "Saccharin" in Wines. By DIOSCORIDE VITALI (*Chem. Centr.*, 1899, i, 1297—1298; from *Boll. Chim. Farm.*, 38, 297—300).—The only trustworthy method is based on the conversion of the sulphur of "saccharin" into sulphate.

Small quantities of "saccharin" may be estimated by precipitation with mercuric nitrate. The precipitate is then weighed and the amount of mercuric oxide in it estimated, the difference representing the "saccharin."

L. DE K.

Employment of Chloral Hydrate in the Estimation of Alkaloids. By EDUARD SCHAEER (*Zeit. anal. Chem.*, 1889, 38, 469—472).—The author completely confirms Lenz's opinion (*Abstr.*,

1899, ii, 391) as to the value of chloral hydrate for the extraction of the vegetable alkaloids from plant products, especially when large proportions of resins and ethereal oils are present. A still more powerful solvent, especially for solid fats and waxes, is a concentrated alcoholic solution of chloral alcoholate. Mauch has made the observation that the salts of the alkaloids are dissolved by aqueous chloral hydrate as readily as the free bases. A difficulty is, however, encountered in the extraction of strychnine from nuxvomica seeds and Ignatius beans, in consequence of the presence of mucoid compounds, which (in common with certain varieties of starch and also animal gelatin) swell up in chloral hydrate, and render it viscous. Caoutchouc and gutta percha also resist completely the solvent action of chloral hydrate, and, when they are present to a large extent, no advantage results from the use of chloral.

Mauch asserts that when the chloral hydrate solutions of the bases are warmed, the bases are often converted into formates. So far as the author's experience extends, the chloral solutions of the alkaloid salts exhibit great permanence, and, may be heated on the water-bath without loss of alkaloid.

M. J. S.

The Chromic Acid Test for Cocaine. By GEORGE L. SCHAEFER (*J. Amer. Chem. Soc.*, 1899, 21, 936—938. Compare Abstr., 1899, ii, 715).—In reply to the criticisms of Squire (*Chemist and Druggist*, April 22), Cownley (*Pharm. J. Trans.*, April 15), and Merck (*Pharm. Zeit.*, No. 42), the author upholds his own chromate process.

L. DE K.

The Active Principle of Cayenne Pepper. By KARL MICKO (*Chem. Centr.*, 1297; from *Zeit. Unters. Nahr.-Genußsm.*, 2, 411—412. Compare Abstr., 1899, i, 716).—Capsacutin described by Mörbitz is probably the same compound as the author's capsaicin, $C_{18}H_{13}O_3N$, the active principle of *Capsicum annuum*, L., and *Capsicum fastigiatum*, Bl.

Reactions of capsaicin.—When moistened with neutral solution of ferric chloride and a little alcohol, insoluble, greenish-blue drops are noticed, but this test is not particularly delicate. Strong sulphuric acid and a particle of sugar cause, after some hours, a fine violet coloration. When heated on the water-bath with strong hydrochloric acid, an alkaloidal substance is obtained which yields precipitates with platinic chloride, iodine, and potassium mercuric iodide.

L. DE K.

Detection of Nucleo-albumin in Urine by means of Tannin. By LÉON GARNIER and L. MICHEL (*J. Pharm.*, 1899, [vi], 10, 150—152).—The precipitate produced when tannin (Almén's reagent) is added to urine previously diluted with its own volume of a saturated solution of sodium chloride, consists chiefly of tannin with a small amount of sodium chloride and traces of nitrogenous substances. The phosphates present in the urine cause the precipitation of the tannin. Ott's statement (*Jahresber. für Thierchemie*, 1895, 567) that the formation of this precipitate is a sure test for the presence of nucleo-albumin is thus proved to be erroneous.

H. R. LE S.

Estimation of the Products of Digestion with Pepsin. By JEAN EFFRONT (*Chem. Zeit.*, 1899, 23, 770—771 and 783—784).—A solution of tannin in tartaric acid may be employed for separating proteoses and peptones, as proteoses are precipitated and peptones remain in solution; its use is suggested as a reagent in the analysis of the products of peptonisation. For a complete analysis, the following determinations should be made: 1, total nitrogen; 2, total proteids; 3, syntonins; 4, proteoses; 5, peptones. For the total proteids, the solution is precipitated with phosphotungstic acid, the precipitate washed with $N/2$ hydrochloric acid and dried without removal from the filter; the nitrogen in this precipitate is estimated, and the number thus obtained multiplied by 6.25 gives the total proteids. Syntonins may be estimated by exactly neutralising the solution with sodium hydroxide (1:10), or even more correctly by estimating the total proteids in the original solution and then in the neutralised solution, the difference between the two determinations giving the percentage of syntonins. Proteoses may be precipitated by a tartaric acid solution of tannin after the albumin is first removed by coagulation, and the syntonins by neutralisation. The solution is made by dissolving tannin (50 grams) in water (500 c.c.) adding N -sodium hydroxide (50 c.c.), making up to 1 litre, and then adding 15 c.c. of a 10 per cent. tartaric acid solution. The precipitate is well washed, then dried between filter-paper, and the percentage of nitrogen determined. The peptones which remain in solution may be precipitated by phosphotungstic acid.

The percentages of peptoses obtained by salting out with zinc sulphate, and by precipitating with a tartaric solution of tannin, are not concordant when the proteid solution has undergone an appreciable amount of peptonisation.

The results obtained also indicate that phosphotungstic acid is an uncertain reagent for estimating peptones. It appears that, after prolonged peptonisation, the peptones are no longer precipitated by this reagent, and it is concluded that the compounds known as peptones are really substances of very different characters, some of which are precipitated by the phosphotungstic acid reagent and others not, and, further, that peptones themselves are acted on by pepsin.

The process of analysis described above gives accurate results only when peptonisation has proceeded for a short time. J. J. S.

Analysis of Glue and Leather. By WILHELM FAHRION (*Chem. Zeit.*, 1899, 23, 452—453).—Glue and leather contain a small quantity of fatty matter, which, however, is partially oxidised, and incompletely soluble in light petroleum. To estimate fat in glue, 10 grams of the cut-up sample are heated with 40 c.c. of 8 per cent. alcoholic potash on the water-bath, adding some more alcohol if necessary, and finally evaporating to dryness. The residue is then dissolved in hot water and rendered acid with hydrochloric acid. The liquid is heated nearly to boiling for half-an-hour, then transferred to a separating funnel, and, when cold, shaken with ether and then left to settle overnight. The aqueous layer is drawn off, the ether poured off, and the hydroxy-acids which adhere to the sides of the funnel are dissolved in hot

alcohol. Both the ethereal and alcoholic solutions are then evaporated in the same tared dish.

Alcoholic potash is also useful in leather analysis. The rasped sample is first extracted with light petroleum to obtain the bulk of the fat. It is then treated with alcoholic potash as described, but on faintly acidifying with hydrochloric acid, a precipitate of tannin and its derivatives (phlobaphens) is obtained which occludes some more fat, and also any hydroxy-acids. The fat may be extracted with ether, but as yet a process is not known for the separation of fatty hydroxy-acids from the tannin precipitate. The latter may be dried and weighed, but as it always contains mineral matters, it must be finally burnt to ash.

L. DE K.

Estimation of Humus in Soils. By C. ASCHMAN and HAROLD FABER (*Chem. Zeit.*, 1899, 23, 61).—25 grams of the finely divided air-dried sample are put into a porcelain dish and heated for 1 hour on the boiling water-bath with 100 c.c. of aqueous caustic soda (50 grams per litre); the liquid is poured off and the extraction repeated several times. The whole, including the deposit, is then made up to 510 c.c. (10 c.c. being occupied by the insoluble matter) and after the supernatant liquid has become clear, an aliquot part is syphoned off and tested as follows: 0.125 gram of humic acid (*acid. huminic. pur.*) is dissolved in soda solution and diluted to 500 c.c.; 5 c.c. are diluted to 100 c.c., 10 c.c. of dilute sulphuric acid (1:5) added, and the liquid boiled with addition of solution of potassium permanganate (0.32 gram per litre) until the colour is no longer discharged. 10 c.c. of a solution of oxalic acid (0.63 gram per litre) are now added and the excess of oxalic acid titrated back with the permanganate solution. The usual blank experiment is then made, and having thus found the humic acid value of the permanganate, the amount of humic acid in the soil may be ascertained by titration. For the success of the experiment, it is necessary that the amount of the humic acid present in the aliquot part of the solution of the sample shall not materially differ from the amount used in the standardising experiment.

L. DE K.

Analyses of Ginger. By EDWY G. CLAYTON (*Analyst*, 1899, 24, 122—125).—The author has analysed 37 samples of ginger from various sources (some of them being again analysed after steeping in water or proof spirit) and has tabulated the results.

The analysis comprises the following estimations: soluble and insoluble ash; the extracts obtained with cold water, ether, absolute alcohol (after complete extraction with ether), and light petroleum respectively; essential oil; alkalinity calculated as potash, and chlorine in the soluble ash; in certain cases, the ash, alkalinity of the ash, chlorine in the cold water extract, water, and silica were also determined.

It appears that the commercial processes—washing, scraping, cutting, grinding, and separation of fibre—do not so alter the composition of genuine ginger as to convey the idea that it has been adulterated with spent ginger, except in some cases where excessive washing had occurred.

L. DE K.

General and Physical Chemistry.

Electrical Conductivity of Alkali Chlorides and Nitrates. By FRIEDRICH KOHLRAUSCH and MARGARET E. MALTBY (*Chem. Centr.*, 1899, ii, 465—466; from *Sitz. Kgl. Akad. Wiss. Berlin*, 1899, 665).—With the view of testing the theoretical connection between molecular conductivity and ionic migration, the conductivities in dilute solution of the chlorides and nitrates of potassium, sodium, and lithium have been determined with the greatest care. The numbers in the following table give the equivalent conductivities at 18° for solutions of the concentration m , and represent the mean of several determinations, which agreed on the average to 1/4000th.

m .	KCl.	NaCl.	LiCl.	KNO ₃ .	NaNO ₃ .	LiNO ₃ .
0·0001	129·05	108·06	98·06	125·49	104·53	94·38
0·0002	128·76	107·80	97·78	125·18	104·18	94·07
0·0005	128·09	107·18	97·13	124·44	103·53	93·45
0·001	127·33	106·48	96·45	123·64	102·85	92·80
0·002	126·29	105·55	95·55	122·59	101·88	91·91
0·005	124·40	103·79	93·86	120·47	100·07	90·27
0·01	122·42	101·95	92·08	118·20	98·16	88·55
0·02	120·00	99·66	89·88	115·27	95·70	86·38
0·05	115·94	95·86	86·22	110·09	91·60	82·86
0·1	112·00	92·01	82·35	104·77	87·24	79·24
0·2	107·96	87·73	77·93	98·74	82·28	75·06
0·5	102·40	80·93	70·65	89·23	74·05	68·03
1·0	98·28	74·34	63·30	80·47	65·86	60·80

For solutions up to and including the concentration $N/500$, each ion has a specific conductivity, which depends on the concentration alone; up to $N/10$ solution, the deviations from this rule amount to ± 1 per cent. As a rule, the fall of ionic conductivity with increasing concentration is most rapid in the case of ions with high migration velocity, but no general and simple law can be laid down. Within the same limits, the fall of conductivity is, in the cases of potassium and sodium, more rapid for the nitrate than for the chloride; in the case of lithium, more rapid for the chloride than for the nitrate.

J. C. P.

Change of Free Energy in Fused Halogen Compounds of some Heavy Metals. By RICHARD LORENZ (*Zeit. anorg. Chem.*, 1899, 22, 241—255. Compare Abstr., 1899, ii, 269).—In determining the E.M.F. of polarisation for a number of fused salts (Abstr., 1899, ii, 267), Czepinski found the temperature coefficient abnormally large at higher temperatures. Further investigation by Weber (Abstr., 1899, ii, 724) has shown that this coefficient dE/dT is regular, even up to high temperatures, when the electrodes are kept far enough apart; the necessity for this is due to the diffusing and penetrating power of the halogen and the metallic vapour.

Differentiation of the equation $E = Q + T.dE/dT$ leads to the relation $-dQ/dT = T.d^2E/dT^2$. Thus, when dE/dT is constant, Q must also be constant. This relation is approximately fulfilled in the case of lead chloride, so that the molecular heat of the compound is very nearly the sum of the atomic heats of the components. On the assumption that this relation holds exactly, the E.M.F. may be extrapolated for ordinary temperatures. The value thus calculated for the E.M.F. of the system $Pb | PbCl_2 | Cl_2$ is 1.65 volts, agreeing with the value 1.59 volts for the E.M.F. of decomposition of lead chloride in solution, calculated by Bodländer from its solubility.

The paper also discusses the ionic concentrations in fused salts, leading to the conclusion that the dissociation of fused silver chloride is rather more than twice that of fused lead chloride. J. C. P.

Coagulative Power of Electrolytes. By W. C. DAMPIER WHETHAM (*Phil. Mag.*, 1899, 48, 474—477).—The coagulative power of an electrolyte may be taken as inversely proportional to the number of gram-equivalents necessary to produce immediate coagulation in a given solution of a colloid. The coagulative powers of sulphates with uni-, bi-, and ter-valent ions stand in the ratio 1:35:1023 (compare *Trans.*, 1895, 67, 63), those of chlorides in the ratio 1:30:1650. There is certainly an intimate connection between the coagulative power and the electrical properties of a solution, and it may be supposed that to produce coagulation a certain minimum electrical charge is necessary. Further, as the electrical charge on an ion is proportional to its valency, equal charges are carried by $2n$ triads, $3n$ dyads, or $6n$ monads. On this basis, it is shown that the coagulative powers of uni-, bi-, and ter-valent ions in equivalent solution are in the ratio $1:x:x^2$, agreeing well with the numbers just quoted. If this view is correct, the coagulative power of a quadri-valent metallic sulphate would be about 30,000 times as great as that of a sulphate with a univalent ion. J. C. P.

Application of the Dissociation Theory to the Electrolysis of Aqueous Solutions of Two Electrolytes with One Common Ion. By JAMES G. MACGREGOR (*Chem. Centr.*, 1899, ii, 82; from *Trans. Roy. Soc. Canada*, [ii], 4, 117—148).—The author has calculated the values of the dissociation in solutions of mixed electrolytes with one common ion, and obtained from these values the ratio of the transference numbers of the other two ions, the values so resulting being compared with those obtained by Hopfgartner (*Abstr.*, 1898, ii, 151). The agreement was satisfactory in the cases of solutions of sodium and hydrogen chlorides, potassium chloride and iodide, and barium and hydrogen chlorides. Agreement was not obtained in the case of solutions of copper and hydrogen sulphates, but this is explicable by the dissociation of the acid into H and HSO_4 ions as well as into H_2 and SO_4 ions. L. M. J.

Theory of the Electrolytic Solution Pressure. By R. A. LEHFELDT (*Phil. Mag.*, 1899, 48, 430—433).—The electrolytic solution pressure, Π , of a metal is calculated from the observed E.M.F.

between the metal and the solution in which it is immersed by the equation $E = RT/\epsilon \log_e \Pi/P$, where ϵ is the quantity of electricity associated with 1 gram-equivalent, and P is the osmotic pressure of the metallic ions in the solution. For zinc, Π has the very high value 9.9×10^{18} atmospheres. An expression is obtained for the tension due to the electrical double layer between the metal and the ions in solution, leading to the equation, $x = \sqrt{D\Pi/2\pi\epsilon^2}$, where x is the number of gram-equivalents that go into solution per sq. cm. of surface, and D the dielectric constant of the medium. From this equation, it may be shown that in order to produce the solution pressure attributed to zinc, 1.27 grams of the metal would have to pass into the ionic form per sq. cm. immersed, a conclusion which is not borne out by observation. Besides this difficulty with regard to the electrolytic solution pressure of zinc, there is one of another kind in the case of palladium, for which $\Pi = 1.5 \times 10^{-36}$; the smallness of this value involves the rejection of the molecular theory of fluids.

J. C. P.

Thermal Conductivity in Gases. By M. SMOLUCHOWSKI R. VON SMOLAN (*Chem. Centr.*, 1899, ii, 353, from *Oesterr. Chem. Zeit.*, 2, 385).—It has been previously shown that, as foretold by Maxwell, the thermal conductivity of a gas is independent of pressure. The author shows, however, that this does not hold for very low pressures, and in this case a temperature difference occurs at the surface of gas and solid. When the mean wave-length is greater than the dimensions of the containing vessel, the phenomena are very complicated. Brush's assumption of the existence of etherion is not justified, and the author considers the supposed element to be merely aqueous vapour (compare *Abstr.*, 1899, ii, 287).

L. M. J.

Thermal Capacity and Colour Changes of Solutions of Cobalt Chloride. By M. WREWSKY (*Chem. Centr.*, 1899, i, 1202; from *J. Russ. Chem. Soc.*, 1899, 31, 164—171).—Owing to difficulties in calorimetry at high temperatures, the changes in colour were brought about by the addition of alcohol. The change from a blue to a red solution is accompanied by an increase in the difference between the thermal capacities of solution and solvent. The author considers the results support Berthelot's hydrate theory. The decrease of thermal capacity by dissolution of salts is a function of both concentration and temperature, increase of both acting in the same sense.

L. M. J.

NOTE BY ABTRACTOR.—With regard to the comparison of the heat capacities of a solution and its components, see Tammann, *Abstr.*, 1896, ii, 289.

Thermal Capacity of Solutions of Sulphuric Acid. By EUGEN VON BIRON (*Chem. Centr.*, 1899, i, 1202—1204; from *J. Russ. Chem. Soc.*, 1899, 31, 171—203).—The author has determined the mean specific heat between 18.6 and 21.8 for solutions of sulphuric acid of the composition H_2SO_4, nH_2O , where n varies from 0 to 1600, the extreme values for these liquids being 0.3352 and 0.99675. The molecular heat for the monohydrate is 51.17, that calculated from its

components being 50.9, and the difference is ascribed to the heat of dissociation of the hydrate. At dilutions greater than $\text{H}_2\text{SO}_4, 100\text{H}_2\text{O}$, a linear relationship is found to exist between the equivalent electrical conductivity and the difference between the found and calculated values for the molecular heat, so that it appears probable that both owe their origin to the same cause (compare Tammann, *Abstr.*, 1896, ii, 289).
L. M. J.

Some Boiling Point Curves. II. By JOHN K. HAYWOOD (*J. Amer. Chem. Soc.*, 1899, 21, 994—1001).—A continuation of the author's previous paper (*Abstr.*, 1899, ii, 632), the mixtures examined being benzene with chloroform, carbon tetrachloride, ether, acetone, and methyl alcohol; and methyl alcohol with ethyl alcohol, carbon tetrachloride, and ether. Minima were obtained in the following cases at the temperatures and composition given: benzene with methyl alcohol, 58.3° ; 53 to 67 per cent. of benzene; methyl alcohol with carbon tetrachloride, 55.95° , about 18.4 per cent. of alcohol. The law previously suggested that chemically similar substances yield similar boiling point curves again receives support, whilst it also appears that similarity of constitution of the two mixed compounds is unfavourable to the production of a minimum even when the boiling points are close together.
L. M. J.

Liquid Mixtures of Constant Boiling Point. By GARNETT RYLAND (*Amer. Chem. J.*, 1899, 22, 384—396).—A mixture of methyl alcohol and benzene containing 38 per cent. of alcohol distils at the constant temperature $57-57.5^\circ$; similarly, a mixture of ethyl alcohol and benzene with 32 per cent. of alcohol distils unchanged at $67-68^\circ$. The composition of the mixture with constant boiling point is in both cases dependent on the pressure.

Numerous binary mixtures of organic liquids have been examined with the view of discovering mixtures of constant boiling point. Forty-five have been found to boil at a constant temperature at or below the boiling point of the more volatile constituent, two above the boiling point of the less volatile constituent, and one between the boiling points of the constituents. For these mixtures of constant boiling point, the ratio of the two constituents in the distillate is approximately that of the products of their vapour density and vapour tension at the temperature of distillation, a result in accordance with earlier researches on the subject.
J. C. P.

Melting Points in Systems of Optical Isomerides. By H. W. BAKHUIS ROOZEBOM (*Proc. K. Akad. Wetensch. Amsterdam*, 1899, 1, 466—468).—Melting point curves for mixtures of the racemic and dextro-compounds were examined in the case of dimethyl tartrate and dimethyl diacetyltartrate. In the first case, the racemic compound melts at 89.4° and the active compound at 43.3° , and a minimum of 41.6 is reached at 3 per cent. of racemic compound; in the second case, the melting point of the racemic compound is 83.8° and that of the active compound 104.3° ; the minimum of 83.4° is reached at about 86 per cent of the racemic compound. In both cases, the form of the curve is almost horizontal at the racemic compound, and indicates

considerable dissociation. The results confirm the author's previously published theoretical views (Abstr., 1899, ii, 401). L. M. J.

Freezing Point of Mixtures of Acetic Acid and Water. By ALBERT DAHMS (*Ann. Chim. Phys.*, 1899, [vii], 18, 140—142. Compare Abstr., 1897, ii, 245; 1899, ii, 546).—Coppet's determinations of the freezing points of dilute acetic acid agree closely with the values previously obtained by the author, who has also anticipated the theoretical conclusions deduced by this investigator. G. T. M.

Freezing Point of Mixtures of Acetic Acid and Water. A Reply. By LOUIS C. DE COPPET (*Ann. Chim. Phys.*, 1899, [vii], 18, 142—144).—The author, whilst admitting that Dahms first determined the freezing point of the eutectic mixture of acetic acid and water, claims to have discovered the lower freezing point of a superfused mixture at a temperature about 2° lower than the eutectic point. The author's conclusions were originally published over 27 years ago.

Since binary liquid mixtures having two eutectic points and three freezing points are known, it is highly probable that similar mixtures having three or more eutectic points should be capable of existence.

G. T. M.

Test by Freezing Point Determinations of the Dissociation Values obtained by the Conductivity Method in the case of Solutions of Potassium and Sodium Sulphates. By E. H. ARCHIBALD (*Chem. Centr.*, 1899, ii, 7, and *Chem. News*, 1899, 80, 46, *et seq.*; from *Trans. Nova Scotia Inst.*, 10, 33).—Determinations were made of the electrical conductivity of solutions of each of the compounds at various dilutions at 18° and at 0° . In the case of potassium sulphate solutions at concentrations above 0.35, the dissociation is slightly greater at 0° than at 18° . The cryoscopic depressions of the solutions were also determined by the method adopted by Loomis, with whose results also the values are in good accord. Comparison of these depressions with those calculated from the dissociation values show the agreement to be close, the differences never exceeding 4 per cent., being, however, for the sodium chloride always in the same directions. For mixtures of equal volumes of solutions containing molecular proportions of the two salts, the depression is given by the expression $D = 1.86, (1 + a_1 + a_2)N/2$, where N is the number of gram-equivalents per litre of each salt in the solutions mixed, and a_1, a_2 the dissociation [this expression appears to involve the assumption that the salts are *equally* dissociated, which is, however, almost the case for the salts examined], and the depressions so calculated are found to agree well with those determined experimentally. L. M. J.

Cryoscopic Behaviour of Substances with Constitutions similar to that of the Solvent. V. By FELICE GARELLI and F. CALZOLARI (*Gazzetta*, 1899, 29, ii, 357—375. Compare Abstr., 1899, ii, 732).—The cryoscopic behaviour of various substances has been studied in solvents, from which they are derived by the substitution of an amino- or a hydroxyl group for a hydrogen atom. In the following cases, abnormal molecular weights were obtained, indicating the formation of solid solutions between the solvent and the solute; *p*-hydroxy-

azobenzene and *p*-aminoazobenzene dissolved in azobenzene; *m*-nitro- and *p*-nitro-phenol and *o*-nitro-, *m*-nitro-, and *p*-nitro-aniline in nitrobenzene; 2:4-dinitroaniline in *m*-dinitrobenzene; *p*-xylydine in *p*-xylene; *p*-hydroxyacetophenone in acetophenone; triphenylcarbinol in triphenylmethane; and glycollic acid in acetic acid. With solutions of *o*-nitrophenol in nitrobenzene, 2:4-dinitrophenol in *m*-dinitrobenzene, and *p*-aminoacetophenone in acetophenone, normal molecular weights are obtained.

T. H. P.

Influence of the Solvent on the Cryoscopic Behaviour of Phenols. By KARL AUWERS [with W. BARTSCH and H. M. SMITH] (*Zeit. physikal. Chem.*, 1899, 30, 300—340).—If the abnormal cryoscopic depressions of hydroxy-compounds are due to association, then an association constant should be obtainable by a calculation similar to that used for obtaining the dissociation constant. Experiments with acetoxime, benzophenoxime, *l*-camphoroxime, benzoic acid, and *o*-bromobenzoic acid, however, show that, except in the last case, no constant value for the association constant is obtained, at least not on the assumption of double molecules. Determinations with other compounds to high concentrations further show that the molecular weight does not, in general, tend to any constant value; the greatest value of association hitherto observed is about four, whilst cryoscopic depressions of ethyl alcohol in benzene give values leading to seven times the normal molecular weight. It appears, therefore, that the abnormal depressions are not due to association, but to some mutual influence of solvent and solute, and determinations were made of the depressions of a number of hydroxy-compounds in various solvents. The following were employed as solvents, and the cryoscopic constant obtained for each is added:—Nitrobenzene, 70; *m*-dinitrobenzene, 106; *p*-nitrotoluene, 78; 2:4-dinitrotoluene, 89; 2:4:6-trinitrotoluene, 115; *p*-chloronitrobenzene, 109; *p*-dichlorobenzene, 77; *p*-chlorobromobenzene, 92; *p*-dibromobenzene, 124; benzil, 105. In all these solvents, ortho-substitution derivatives of phenol were cryoscopically normal as in benzene or naphthalene; with para-compounds, however, this is not the case, *p*-nitrophenol, methyl *p*-hydroxybenzoate, and *p*-hydroxybenzaldehyde being abnormal in the halogen compounds, but almost normal in those solvents containing a nitro-group, so that the halogen increases and the nitro-group decreases the abnormalising influence in the solvent. Other substituted phenols dissolved in *p*-dichloro-, *p*-chlorobromo-, and *p*-dibromo-benzene were then investigated, and it was found that, as in naphthalene, para-compounds are more abnormal than meta-, and the order of the groups arranged according to their influence in giving abnormal values is: aldehyde, cyanide, substituted carboxyl, nitro-groups, whilst the abnormality is greatest in dichlorobenzene, and least in dibromobenzene. The abnormal cryoscopic depressions are hence the product of two factors, one dependent on the constitution of the solute, the other on that of the solvent (compare Abstr., 1896, ii, 293; 1897, ii, 476). L. M. J.

Influence of the Medium on the Heats of Solution of Salts. By N. GALITZKI (*Chem. Centr.*, 1899, ii, 469—470; from *J. Russ. Chem. Soc.*, 31, 536—540).—The effect of increasing quantities of alcohol on

the heats of solution of potassium nitrate and potassium carbonate in water has been investigated. By the addition of alcohol to water, the heat of solution is diminished, the diminution ultimately reaching a minimum, which depends on the nature of the dissolved salt. No connection could be traced between this phenomenon and the electrical conductivity of the solutions. J. C. P.

The Critical State. By KONRAD DIETERICI (*Ann. Phys. Chem.*, 1899, 69, 685—705).—For most substances hitherto investigated, the ratio of the actually observed critical density to the ideal density (the density which the substance would have if the law $pv = RT$ held for the critical pressure and temperature) is nearly constant, and equal to 3.75; for ethylene, nitrous oxide, nitrogen, and oxygen, the ratio differs considerably from 3.75, but this is probably due to deficient experimental methods.

In van der Waals' equation, the cohesion pressure is equal to a/v^2 , and the correction for the molecular volume is a constant b ; in these circumstances, the ratio v_0/v_k (ideal volume: critical volume) has the value 2.67. This want of correspondence between experiment and van der Waals' equation remains, even when b is regarded as a function of v .

If the equation $(p + \pi)(v - b) = RT$ be accepted, and the cohesion pressure $\pi = a/v^{5/3}$ instead of a/v^2 , the ratio v_0/v_k is equal to 3.75. This purely empirical law regarding the cohesion pressure, although it brings van der Waals' equation into agreement with the critical phenomena, is without theoretical basis.

Other theoretical considerations lead to the equation $p = RT/(v - b) \cdot e^{-A/RT}$, where A is a function of v , and represents the work to be done by a molecule against the forces of cohesion. On the supposition that $A = C/v$, the ratio v_0/v_k is equal to 3.695, a value agreeing closely with that given by experiment. J. C. P.

Hydrolytic Dissociation in Salt Solutions. By HEINRICH LEY (*Zeit. physikal. Chem.*, 1899, 30, 193—257).—In a salt solution, besides the electrolytic dissociation, hydrolysis may occur with the formation of acid and base which further undergo electrolytic dissociation. The concentrations of the various molecular groupings present in the solution are determined by the equilibrium constants for the hydrolytic dissociation and for the electrolytic dissociation of salt, acid, base, and water. The author first investigates theoretically the necessary equations for the cases where (1) either base or acid is weak; (2) both acid and base are weak. For the determination of the hydrolysis, the method of sugar inversion was found suitable, and the author obtains the value 16.8 for the inversion constant at 100°, which is thus intermediate between the values 17.9 found by Trevor (*Abstr.*, 1893, ii, 62) and 16.0 found by Smith (*Abstr.*, 1898, ii, 155). The variation of the constant with temperature was also determined and found to be given by the expression $K_{T_1} = K_{T_0} e^{A(T_1 - T_0)/T_1 T_0}$, where A is a constant. Some salts were found to cause an irregular increase of inversion, apparently not due to hydrolysis, as, for example, lanthanum chloride. Lithium and magnesium salts have no effect, but beryllium and aluminium cause considerable inversion, and for these the hydrolytic constant was calculated at dilutions from 32 to

512. The values do not remain constant, but the author considers the agreement to be satisfactory, owing to the complicated equations and the fact that they are rigorously valid for only binary electrolytes. From the values of the dissociation, the basicity of the hydroxides may be compared, and it is thus found that beryllium hydroxide is about eleven times as strong a base as aluminium hydroxide. Salts of cerium, copper, and zinc are only very slightly hydrolysed; lead causes greater inversion, but still far less than the aluminium salts. The hydrolysis of methyl acetate was also employed for the determinations, and the values for the hydrolysis of aluminium chloride by this process agree well with those obtained by the inversion method. Conductivity determinations may also serve for the calculation of hydrolysis; the acetates of manganese, cobalt, zinc, and nickel exhibit a perfectly normal change of conductivity with dilution, and are hence not hydrolysed. With acetate of lanthanum, cerium, and lithium, this is not the case, whilst acetates of lead, beryllium, aluminium, and mercury give very abnormal results, indicating considerable hydrolysis. Where quantitative results were obtained, the values of percentage hydrolysis at $v=1024$ and 25° are: beryllium sulphate, 5 per cent.; aluminium chloride, 4.5 per cent.; lead chloride, 4.4 per cent.; uranium nitrate, 5.9 per cent.; mercuric perchlorate ($v=512$), 37 per cent. (Abstr., 1898, ii, 66).
L. M. J.

Determination of Solubility Coefficients of Liquids. By A. AIGNAN and E. DUGAS (*Compt. rend.*, 1899, 129, 643—645).—When aniline and water are mixed, there is no alteration of total volume consequent on the reciprocal solubility of the liquids, and in this case it is possible to determine the solubilities by observation of the volumes of the two layers before and after agitation, in two different experiments. The values so obtained in c.c. per cubic centimetre are: (1) aniline in water, 0.036; (2) water in aniline, 0.042. In the case of water and fermentation amyl alcohol, however, the total volume does not remain constant, and very diverse values for the solubilities, sometimes even negative, are obtained, so that in this case the author considers the case is not one of simple solubility, and the results may be due to the fact that one of the alcohols present in the fermentation amyl alcohol is capable of combining with water.
L. M. J.

Equilibrium between Manganous Salts and Ammonia. By W. HERZ (*Zeit. anorg. Chem.*, 1899, 22, 279—284).—The results previously obtained (Abstr., 1899, ii, 752) were not in harmony with the law of mass action, but it is now found that at lower concentrations the equation $K = [\text{Mn}^{++}][\text{NH}_3]^2/[\text{NH}_4^+]$ gives fairly constant values of K : in this equation, the symbols in square brackets indicate the concentrations of the respective molecules or ions. With the mean value of $K=1.6 \times 10^{-3}$, and the dissociation constant of ammonia $=0.000023$, the solubility of manganous hydroxide is calculated to be 0.6×10^{-4} , a value of the same order as that obtained by Bodländer from other considerations.
J. C. P.

Fusion of Sodium Thiosulphate. Hydrates. By FRIEDRICH WILHELM KÜSTER and A. THIEL (*Zeit. anorg. Chem.*, 1899, 21, 401—404).—Fused sodium thiosulphate might be regarded either as

a definite liquid compound, or as a reciprocal solution of the decomposition products of the crystallised salt. In the first case, excess of water or anhydrous thiosulphate in the fused hydrate would give two distinct series of solutions, the properties of which might be represented by two curves, cutting each other at the point corresponding with the composition $\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$. If, on the other hand, the fused hydrate is merely a reciprocal solution of water and anhydrous salt, its properties ought to be intermediate between those of solutions with excess of water and anhydrous salt respectively. The latter behaviour has been observed in the case of the conductivity. As the number of water molecules to one molecule of anhydrous salt rises from 4.69 to 6.65, the conductivity increases proportionally, and there is no discontinuity whatever corresponding with the composition $\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$.
J. C. P.

Molecular State of Ammonia and of Amines in Aqueous Solutions. By ARTHUR HANTZSCH and F. SEBALDT (*Zeit. physikal. Chem.*, 1899, **30**, 258—299).—In the hope of solving this question, the author determined the partition ratio of ammonia and amines between water and other solvents. Ammonia in water and chloroform was first examined; if it exists as hydroxide, the scheme of dissociation is $\text{NH}_4\text{HO} \rightleftharpoons \text{NH}_3 + \text{H}_2\text{O} \rightleftharpoons \text{NH}'_4 + \text{HO}'$, and as ammonia is but a weak base, the latter dissociation is very slight. The calculation of the partition ratio is made on the assumption that the hydroxide itself is insoluble in chloroform, and as the concentration of the gaseous ammonia in the aqueous phase is proportional to that of the hydroxide, the total concentration may be, and is, employed instead of that of the gaseous ammonia only. The value for the partition ratio, water/chloroform at 25° , is about 25, and remains constant for varying concentrations, but it increases with fall of temperature. The values were not affected by the addition of ammonium chloride, a result the authors consider to be surprising, although, in view of the slight electrolytic dissociation of ammonium hydroxide, it might have been expected. The partition of piperidine between benzene and water and the effect of addition of piperidine hydrochloride, were next examined; the addition of sodium hydroxide was found to cause considerable decrease in the partition ratio, which was also found to decrease with increase of temperature. The partition at various temperatures was also determined for trimethylamine and triethylamine between water and toluene; acetic acid, pyridine, hydrogen cyanide, and cyanacetic acid between water and benzene; and for acetic acid, cyanacetic acid, ferric thiocyanate, and mercurous chloride between water and ether. With the amines, in every case the partition ratio decreases with rise of temperature; this was also the case in a few other systems, but in most the converse obtained. This seems to indicate the existence of hydroxides and an increase of molecular dissociation at higher temperatures, but the authors consider it more probable that hydrates, and not hydroxides, exist in the solutions. In ammonia solutions, the temperature coefficient is very small, and here especially the quantity of hydroxide must be very small.

L. M. J.

Conversion of Mixed Crystals into a Compound. By H. W. BAKHUIS ROOZEBOOM (*Proc. K. Akad. Wetensch. Amsterdam*, 1899, 2, 74—77).—No difference is observable in the melting points of dextro-lævo-, and inactive camphoroxime, or of mixtures in any proportions; the solid mass is further perfectly homogeneous, so that the existence of mixed crystals is confirmed (Forster and Pope, *Trans.*, 1897, 71, 1049), and the melting point curve for the mixture is hence a horizontal line. The transition point to monoclinic crystals varies from 112.6° for 100 per cent. of either compound to 109.4° for the inactive mixture, and the curve is quite symmetrical, and here also mixed crystals are again formed. By cooling still more, a further change takes place, and this occurs at 103° for the inactive mixture, but the temperature is considerably reduced by excess of either component, and could not be observed at all when the percentage rose above 75. In this case, therefore, the mixed crystals become converted into a compound, and the views of Pope (*loc. cit.*) are confirmed (see *Abstr.*, 1899, ii, 401).
L. M. J.

Mixed Crystals of Mercuric Iodide and Bromide. By W. REINDERS (*Proc. K. Akad. Wetensch. Amsterdam*, 1899, 2, 146—148).—The melting point curve of mixed crystals of mercuric iodide and bromide is continuous between the temperatures 236.5° and 255.4° , the melting points of the bromide and iodide respectively. It passes through a minimum at 216.1° , corresponding with a mixture containing 59 per cent. of mols. of the bromide, and at this temperature the crystals deposited have the same composition as the molten mixture; if the latter contains more (or less) bromide than the above-named quantity, the crystals deposited are richer (or poorer) in bromide than the mixture. Below 216° , mixed crystals in all proportions can exist.

At 127° , yellow mercuric iodide is converted into the red modification. By admixture of the bromide, this transition point is lowered and also widened out into a transition-interval determined by two limiting curves, one for the yellow, and the other for the red, crystals. The former of these runs from 127° when no bromide is present to a point on the 0° abscissa corresponding with 33 per cent. of mols. of the bromide; whilst that for the red crystals proceeds from the same starting point and cuts the 0° abscissa in a point indicating the presence of 8.6 per cent. of the bromide molecules. The transition interval was determined partly by observation of the colour change, as this made it possible to determine the composition of red crystals which at a definite temperature change completely into the yellow variety; further, solutions were found by trial, each of which deposits at a particular temperature, both red and yellow mixed crystals. These curves could not be continued below 0° , but their direction shows that, if there is a transition point for mercuric bromide, it must be at a very low temperature; at -83° , no indications of such transition could be found.

Solid mercuric bromide and iodide diffuse into one another at ordinary temperatures, and more so when heated, and the transition temperature of a finely-powdered mixture of them agrees very nearly with that of the mixed crystals of the same composition. T. H. P.

Properties of Flames. By NICOLA TECLU (*J. pr. Chem.*, 1899, [ii], 60, 396—399).—I. A stream of coal gas is allowed to issue from a platinum tube about 12 mm. in length and 2 mm. in diameter, so as to afford a flame of definite dimensions, the pressure of the gas at the point where it enters the tube being registered by means of an alcohol manometer. It is found that on heating the platinum tube by means of a flat flame bunsen burner, if the gas supply is taken directly from the main, the flame suffers a contraction of about 70 per cent., whilst the manometer registers only a small increase in pressure (about 40 mm.). If, on the other hand, the gas is supplied from a small laboratory gas-holder, the flame suffers no appreciable contraction when the tube is heated, but the manometer registers an increase in pressure nearly three times as large as in the former case (about 110 mm.).

The explanation offered is that the disturbances, set up by the sudden increase in bulk which the gas undergoes in coming into contact with the heated tube, are propagated backwards with the velocity of compression waves, and suffer reflection in the small laboratory apparatus, producing pressure in the mass of gas and thus affecting the manometer and serving to maintain the size of the flame; where the enormous technical gasometers are involved, the energy of the waves is minimised or dissipated.

II. An apparatus is described which consists of a modification of that used in the ordinary lecture experiment for demonstrating the reciprocal nature of combustion. A. L.

A Dissolver. By ARTHUR JOHN HOPKINS (*Amer. Chem. J.*, 1899, 22, 407—410).—In this apparatus, a glass tube passing through a doubly-bored indiarubber stopper, fitted to a tall glass cylinder, is connected near the bottom of the latter with one limb of a Y-tube, the lower limb of which is open, whilst the third is connected to a vertical glass tube which reaches up nearly to the stopper, and is there curved downwards. Through the second hole in the stopper passes a tube connected with a filter pump which serves to draw a current of air through the apparatus, the rate of this being regulated by a stop-cock on the tube open to the air. The crystals to be dissolved are placed at the bottom of the cylinder; the saturated solution formed there is withdrawn continuously by the suction in the Y-tube and discharged upon the less saturated solvent at the top, fresh solvent thus being brought continuously in contact with the substance to be dissolved.

W. A. D.

Inorganic Chemistry.

Biological and Chemical Purification of Water. By A. TIXIER (*J. Pharm.*, 1899, [vi], 10, 297—300).—In order to avoid the liberation of free alkali which occurs when potassium permanganate or calcium permanganate is used for the purification of water, the

author uses a solution containing aluminium permanganate and barium permanganate. The solution employed has a specific gravity of 35° B., and contains 290 grams of permanganic acid per litre, and 7 per cent. of alumina. It is added to the water to be purified until a persistent pink coloration is produced ; the water is allowed to remain for 24 hours, and after filtration through a carbon or other filter is fit for consumption.

H. R. LE S.

New Ozone Apparatus. By NICOLA TECLU (*J. pr. Chem.*, 1899, [ii], 60, 402—403).—Several new forms of apparatus for exhibiting the phenomenon of ozone production during electric discharge are figured.

A. L.

Spectrum of Chlorine. By JOSEF M. EDER and EDUARD VALENTA (*Chem. Centr.*, 1899, ii, 358).—The spectrum of chlorine was examined at pressures varying from 10 to 100 mm., a concave grating being employed. The authors confirm Ciamician's observation of the broadening of many lines and increase of brightness of the continuous spectrum by increase of pressure, but no band spectrum was obtained. Very characteristic lines were those of wave-length 4132 in the violet and 3860 in the ultra-violet, and the wave-length of many lines are given which at low pressures are seen to be doubled or trebled ; a line at 3750 does not become broader by increased pressure. L. M. J.

Colour of Chlorine Solutions. By E. H. SARLES (*J. Amer. Chem. Soc.*, 1899, 21, 1038).—When chlorine is passed into ethyl alcohol, the liquid finally separates into a lower yellow layer and an upper layer having a grass-green colour. The green solution has bleaching properties which it, however, loses when uncombined chlorine is removed by a current of air or carbon dioxide. The solvent, which gives a green solution of chlorine, has not been isolated ; it is either easily decomposed or very volatile, since when the liquid has been fractionated several times, the green colour is completely lost and cannot be regained by passing fresh chlorine into the liquid.

J. J. S.

Theory of the Electrolytic Formation of Hypochlorite and Chlorate. By FRITZ FOERSTER (*Zeit. anorg. Chem.*, 1899, 22, 1—32).—Investigation of the formation of hypochlorite and chlorate as a purely chemical process (Abstr., 1899, ii, 278) has prepared the way for a theory of the electrolytic preparation of these substances. A review of the work dealing with the electrolysis of alkali chlorides (compare Oettel, Abstr., 1896, ii, 517 ; Haber and Grinberg, Abstr., 1898, ii, 215 and 365 ; Wohlwill, Abstr., 1899, ii, 213) shows that the following conclusions may be regarded as established. Hypochlorite is formed chiefly by the interaction of the chlorine liberated at the anode with the alkali produced during the electrolysis or previously present : in alkaline solution, hypochlorite can be oxidised to chlorate by a primary anode process ; the formation of chloric acid in the electrolysis of dilute hydrochloric acid is due to the direct oxidation of Cl ions at the anode.

A theory of the secondary electrolytic formation of chlorate is discussed, based on two suppositions ; (1) that in the electrolysis of

neutral alkali chloride solutions, chlorine is continually being liberated at the anode, (2) that the hypochlorite takes part in the electrolysis, and that its ions are discharged at the anode with evolution of oxygen. The known facts regarding the influence of current density, temperature, acidity, and alkalinity, on the formation of chlorate, are largely in harmony with the theory; further experiments to determine the exact nature of the process have been made by Müller (see following abstract).
J. C. P.

Formation of Hypochlorite and Chlorate in the Electrolysis of Alkali Chlorides. By ERICH MÜLLER (*Zeit. anorg. Chem.*, 1899, 22, 33—90. Compare Abstr., 1899, ii, 742).—The supposition that in the electrolysis of neutral alkali chloride solutions the formation of hypochlorite and chlorate depends on the same purely chemical process as in the non-electrolytic formation of these compounds, has several consequences. Experiment on the whole confirms these consequences, and shows that the electrolytic formation of chlorate in neutral alkali chloride solutions consists in the following processes; chlorine is discharged at the anode, and unites with the alkali from the cathode to form hypochlorite; even while the hypochlorite concentration is still small, ClO^- ions are discharged at the anode, forming hypochlorous acid, which in its turn oxidises hypochlorite and chloride to chlorate; at low temperatures, hypochlorite is to a small extent oxidised by anode oxygen.

Experiments in acid and alkaline solutions of the alkali chlorides lead to the conclusion that the electrolytic process in these does not differ essentially from that in neutral solution. The electrolytic formation of chlorate may thus be referred in general to four equations: (1) $\text{Cl}^- + 3\text{HClO} = \text{ClO}_3^- + 3\text{H}^+ + 3\text{Cl}^-$; (2) $\text{ClO}^- + 2\text{HClO} = \text{ClO}_3^- + 2\text{H}^+ + 2\text{Cl}^-$; (3) $\text{Cl}^- + 3\text{O} = \text{ClO}_3^-$; (4) $\text{ClO}^- + 2\text{O} = \text{ClO}_3^-$. In dilute hydrochloric acid, the existence of ClO^- ions is excluded, and in this case the formation of chlorate must take place according to equation (3). In other cases, the processes may be represented in varying degree; thus, when there is no appreciable evolution of oxygen, the chief processes are those indicated by equations (1) and (2); when the evolution of oxygen is considerable, as in strongly alkaline solutions, the formation of chlorate will take place chiefly according to equations (3) and (4).
J. C. P.

Molecular Weights of some Elements and their Derivatives. By GIUSEPPE ODDO and E. SERRA (*Gazzetta*, 1899, 29, ii, 343—353).—The molecular weight of iodine has been determined by the boiling point method, the solvents employed being tetrachloromethane, carbon disulphide, benzene, and ethyl alcohol. The numbers obtained with the first two solvents are sensibly the same as those of Beckmann and Stock (Abstr., 1895, ii, 382). Benzene and ethyl alcohol yielded the respective values 273—279 and 265—327, Beckmann and Stock's numbers being 335—360 and 330—342; the latter results, being corrected for the volatility of iodine, give the values 233—255 and

233—241 respectively. The authors' object to this very large correction being applied, as with slow boiling, the amount of iodine volatilised is very small and scarcely sufficient to colour the vapour of the solvent.

In boiling tetrachloromethane, the sulphur molecule contains 8 atoms up to concentrations of about 3 per cent.; beyond that strength of solution, the results obtained are not concordant.

Phosphorus pentachloride has the normal molecular weight in boiling tetrachloromethane.

Solutions of iodine mono- or tri-chloride in tetrachloromethane give lower boiling points than that of the pure solvent. In the case of the trichloride, this is due to the fact that it sublimates at 70—75°. With the monochloride, dissociation takes place according to the equation $9\text{ICl} = \text{I}_2 + \text{I}_4 + 3\text{ICl}_3$, and the effect of the trichloride in lowering the boiling point is greater than that of the iodine in raising it.

T. H. P.

Action of Arsenious and Antimonious Oxides on Sulphur Monochloride. By GIUSEPPE ODDO and E. SERRA (*Gazzetta*, 1899, 29, ii, 355).—When arsenious oxide and sulphur monochloride are heated together in a reflux apparatus, they react according to the equation: $\text{As}_2\text{O}_3 + 6\text{S}_2\text{Cl}_2 = 4\text{AsCl}_3 + 3\text{SO}_2 + 9\text{S}$. The reaction is complete in about an hour, and on cooling, nearly all the sulphur formed crystallises out and the arsenic trichloride can be separated by decantation.

Analogous reactions take place when antimony or bismuth sesquioxide is substituted for the arsenic compound. T. H. P.

Hydrates of Sulphuric Acid. By EUGEN VON BIRON (*Chem. Centr.*, 1899, ii, 467—468; from *J. Russ. Chem. Soc.*, 31, 517—522).—The author has succeeded in crystallising the hydrate $\text{H}_2\text{SO}_4 \cdot 2\text{H}_2\text{O}$, predicted by Mendeléeff. A solution of the composition $\text{H}_2\text{SO}_4 \cdot 2\text{H}_2\text{O}$, cooled with liquid air, solidifies to an amorphous mass. This mass, if rubbed at rather a higher temperature with a glass rod, becomes crystalline, the thermometer rising at the same time to -35° . The crystals thus obtained may be used to start crystallisation in a solution of the composition $\text{H}_2\text{SO}_4 \cdot 2\text{H}_2\text{O}$ cooled merely to -75° with solid carbon dioxide and ether. Cooling with liquid air is detrimental to the formation of the crystals.

The freezing point of the hydrate was determined in a Beckmann's apparatus of small size, well protected by surrounding tubes, and cooled in a mixture of carbon dioxide and ether. During solidification, the thermometer remained steady for about 10 minutes, until practically no liquid was left, showing that the separation of the solid did not alter the freezing point of the remaining liquid. In solutions which deviated from the composition $\text{H}_2\text{SO}_4 \cdot 2\text{H}_2\text{O}$, the thermometer was steady for only 1—2 minutes. The freezing point of the hydrate is -38.9° ; with the same apparatus, the hydrate $\text{H}_2\text{SO}_4 \cdot 4\text{H}_2\text{O}$ solidified at -69° .

J. C. P.

Polymerisation of Inorganic Chloro-Anhydrides. I. By GIUSEPPE ODDO and E. SERRA (*Gazzetta*, 1899, 29, ii, 318—329. Compare this vol., i, 92).—Determined by the boiling point method, the

molecular weight of phosphorus oxychloride in various solvents is as follows: In tetrachloromethane, 325—362; benzene, 283—309; carbon disulphide, 214—244; chloroform, 159—164; ether, 147—157. The cryoscopic method gives a value 149—152 in benzene. The number corresponding with the formula POCl_3 is 153·5.

The molecular weight of thionyl chloride in boiling chloroform is 229—235 and in freezing benzene 108—110; the formula SOCl_2 requires 119.

Phosphorus oxybromide has a molecular weight of 287—310 in boiling tetrachloromethane and 334—352 in boiling benzene; the cryoscopic method gives a value 293—308 in benzene. The calculated value for POBr_3 is 287. Phosphorus thioc chloride gives the following molecular weights. In boiling tetrachloromethane, 209; in boiling benzene, 236—247; in freezing benzene, 158—161. The calculated number is 169·5.

For sulphur monochloride, the values obtained are, in boiling tetrachloromethane, 169—173, and in boiling benzene, 180—193; the formula S_2Cl_2 requires 135.

Chromyl chloride in boiling tetrachloromethane gives the molecular weight 225—243; in boiling benzene, 441—528; and in freezing benzene, 165—175. The formula CrO_2Cl_2 corresponds with a value 155·5.

The cryoscopic method gives for the molecular weight of sulphuryl chloride in benzene the number 131, the value for SO_2Cl_2 being 135.

T. H. P.

Properties of Solutions of Sodium Nitrite. By JOSEF JURI BOGUSKI (*Chem. Centr.*, 1899, ii, 470; from *J. Russ. Chem. Soc.*, 1899, 31, 543—551).—Sodium nitrite, prepared from the commercial article by crystallising from solutions saturated at 125°, has a yellowish tinge which disappears, however, when the salt is dried over sulphuric acid or washed with alcohol, but even then the colourless salt still forms yellowish solutions. This coloration is due to the presence of a foreign substance. The variation of the sp. gr. with the concentration of solutions of the nitrite is represented by a curve which is very nearly a straight line. The specific refractive index of solutions at 20° may be calculated from the formula $[n]_D = 1.33336 + 0.0011559 P$, where P = percentage of nitrite dissolved. The original paper contains copious data and many tables.

E. W. W.

NOTE.—As to the colour of sodium nitrite and its solutions, compare Divers (*Trans.*, 1899, 75, 86), Groves (*Proc.*, 1898, 222).—EDITORS.

Preparation of Cæsium from the Carbonate. By EDMUND GRAEFE and MORITZ ECKARDT (*Zeit. anorg. Chem.*, 1899, 22, 158—160).—A repetition of Winkler's experiments (*Abstr.*, 1890, 331) on the reduction of alkaline carbonates proves Beketoff's assertion that the reduction to metal takes place more easily as the atomic weight increases. The preparation of cæsium is effected at a lower temperature than that of rubidium or potassium. A mixture in the proportion $\text{R}_2\text{CO}_3 : 3\text{Mg}$ is heated in an iron tube, free from rust, in a slow current of dry hydrogen and the metal, which distils

collected under petroleum; a theoretical yield is obtained. Metallic caesium is silver-white with a yellow tinge, retains its lustre under petroleum, oxidises with development of heat on exposure to the air, then melts and explodes, swims on water, and burns with a reddish-violet flame with liberation of hydrogen. E. C. R.

Calcium and its Compounds. By HENRI MOISSAN (*Ann. Chim. Phys.*, 1899, [vii], 18, 289—343).—A detailed account of work already published (compare Abstr., 1894, i, 313; 1898, ii, 116, 161, 578; 1899, ii, 25, 152, 153, 155, 219, 241, and 418). G. T. M.

Setting of Gypsum. By KARL ZULKOWSKI (*Chem. Centr.*, 1899, ii, 602—603; from *Chem. Ind.*, 22, 349—352).—The setting of the ordinary roasted gypsum is due to the formation of the calcium salt, $\text{S(OH)}_4 \cdot \text{O}_2\text{Ca}$, of hexabasic sulphuric acid by the action of water (2 mols.). Gypsum which has been roasted at a moderate red heat is also capable of taking up water, but on account of its greater density it only combines with 1 mol. of water, forming the calcium salt, $\text{SO(OH)}_2 \cdot \text{O}_2\text{Ca}$, of tetrabasic sulphuric acid. The water has a twofold action, first dissolving the more soluble calcium compound, and then combining with it to form a less soluble compound which separates in a crystalline form and sets to a compact mass. E. W. W.

Preparation and Properties of Crystallised Barium and Strontium Phosphides. By A. JABOIN (*Compt. rend.*, 1899, 129, 762—765).—Crystallised strontium phosphide is obtained by heating a mixture of lampblack and strontium phosphate for 3 or 4 minutes in an electric furnace with a current of 45 volts and 950 amperes, and the barium compound is obtained in a similar way. *Strontium phosphide*, Sr_3P_2 , burns in fluorine at the ordinary temperature, in chlorine at about 30° , in bromine at 170 — 175° , in iodine at a red heat, in oxygen above 300° , and in sulphur vapour at a higher temperature. It is decomposed by carbon at a high temperature, but not by sodium at a red heat; by dilute acids and gaseous hydracids, but not by concentrated acids, nor by hydrogen sulphide or ammonia, nor by organic solvents. It alters rapidly in moist air, is decomposed by water with liberation of hydrogen phosphide, and is violently attacked by oxidising agents. Its sp. gr. is 2.68 and it melts only in the electric furnace. *Barium phosphide*, Ba_3P_2 , has similar properties, but is not so readily attacked; it burns in chlorine at 90° and in bromine at 260 — 300° . Its sp. gr. is 3.183. C. H. B.

Formation of Oceanic Salt Deposits, Particularly of the Stassfurt Beds. XIV. Influence of Pressure on the Formation of Tachyhydrite. By JACOBUS H. VAN'T HOFF and H. M. DAWSON (*Chem. Centr.*, 1899, ii, 401—402; from *Sitzungsber. Akad. Wiss. Berlin*, 1899, 557—562. Compare Abstr., 1899, 759).—The effect of increase of temperature and pressure on the evaporation of sea-water is to cause the separation of new compounds, for when the change of the solubilities of the various compounds affected by the alteration of conditions exceeds certain limits, supersaturation with new compounds is rendered possible. Increase of temperature and pressure results in the formation of kieserite, löweite, kainite, and langbeinite, none of

these compounds being formed when sea water is evaporated at 25° under the ordinary pressure. The salt basins of Besançon have a temperature of 62° at a depth of 1·35 metres, and reckoning on this basis the variations of temperature and pressure in the case of the Stassfurt beds which have a maximum depth of 1500 metres amount to 40 and 180 atmospheres respectively.

The effect of changes of temperature and pressure has been investigated in the case of the formation of tachyhydrite (MgCl_3)₂Ca, 12H₂O, which easily separates from mixed solutions of the hexahydrates of magnesium and calcium chlorides at 22°. Experiments with the manocryometer and Beckmann's thermometer show that an extra pressure of one atmosphere only raises the temperature of the formation of tachyhydrite by 0·017°. This effect is comparable with that of pressure on melting points; it lies between the raising of the melting point of ice by 0·0073° and that of paraffin by 0·035° caused by a pressure of one atmosphere. Hence, since an increase of pressure of 180 atmospheres would only raise the temperature of formation by 3°, the effect of increase of temperature must be of much greater importance.

E. W. W.

Solution of Copper in Gelatin Solutions. By ALEXANDER P. LIDOFF (*Chem. Centr.*, 1899, ii, 471; from *J. Russ. Chem. Soc.*, 1899, 31, 571—572).—From the results of experiments on the action of copper salts on alkaline solutions of albumin, it appears that the biuret reaction really depends on the dissolution of copper, the copper salt being reduced to soluble colloidal copper. An alkaline solution of gelatin in which copper gauze was placed had acquired a violet coloration after remaining a day, and after 48 days 3·54 per cent. of the copper was found to have been dissolved.

E. W. W.

Manganese Trichloride and Tetrachloride. By RICHARD JOS. MEYER and HANS BEST (*Zeit. anorg. Chem.*, 1899, 22, 169—191).—The dark green solution of oxides of manganese in hydrochloric acid contains manganese trichloride. Each of the oxides, Mn₂O₃, Mn₃O₄, or MnO₂, when dissolved in absolute alcohol or ether saturated with hydrogen chloride, yields a solution of manganese trichloride which is decomposed by water and also by evaporation in a vacuum over sulphuric acid, and consequently the trichloride cannot be isolated. It, however, yields very characteristic double salts with pyridine and quinoline hydrochlorides which crystallise in lustrous needles.

The action of hydrogen bromide on the oxides of manganese results in the formation of the dibromide which yields a crystalline double salt with pyridine hydrobromide.

When potassium permanganate is boiled with acetic acid, carbon dioxide is evolved and a brown solution obtained, which on cooling deposits the salt, $3\text{MnO}_2, \text{Mn}_2(\text{C}_2\text{H}_3\text{O}_2)_6 + 2\text{C}_2\text{H}_4\text{O}_2$, and if a small quantity of water is added to the mother liquor, Christensen's triacetate, $\text{Mn}_2(\text{C}_2\text{H}_3\text{O}_2)_6 + 4\text{H}_2\text{O}$, crystallises out. The solution obtained by reducing potassium permanganate with acetic acid with the addition of 1 mol. of potassium acetate, when saturated with hydrogen chloride yields the double salt $\text{MnCl}_3, 2\text{KCl}$ (Rice, *Trans.*, 1898, 75, 258). If, however, the solution is only partially saturated with

hydrogen chloride, the salt $\text{MnCl}_4 \cdot \text{MnCl}_3 \cdot 5\text{KCl}$ is obtained. When the acetic acid solution of potassium permanganate, without the addition of potassium acetate, is saturated with hydrogen chloride, a small quantity of the salt $\text{MnCl}_4 \cdot 2\text{KCl}$ is obtained as a black, crystalline precipitate, and the mother liquors contain large quantities of manganese trichloride. The corresponding ammonium salts could not be isolated, although the reaction proceeds apparently in a similar manner. Cæsium permanganate, under similar conditions, yields the salt $\text{MnCl}_3 \cdot 2\text{CsCl}$. Thallium permanganate does not yield a double salt.

The double sulphate, $\text{Mn}_2(\text{SO}_4)_3 \cdot \text{K}_2\text{SO}_4$, is precipitated quantitatively by adding sulphuric acid to the solution of potassium permanganate in acetic acid.

The higher chlorides of iron, cobalt, and nickel are not obtained by the above method. Lead dioxide, when dissolved in cold alcohol saturated with hydrogen chloride, is converted into the tetrachloride, which yields crystalline double salts with pyridine, di- and tri-methylamine hydrochloride, and tetramethylammonium chloride.

Thallium permanganate, TlMnO_4 , forms large, nearly black prisms.
E. C. R.

Atomic Weight of Cobalt. III. Analysis of Cobaltous Chloride and Cobaltous Oxide. By THEODORE W. RICHARDS and GREGORY P. BAXTER (*Zeit. anorg. Chem.*, 1899, 22, 221—234. Compare Abstr., 1898, ii, 377, and 1899, ii, 753).—The authors have determined the weight of the cobalt obtained from a known weight of cobaltous chloride by reducing it in a current of hydrogen. The methods employed are essentially the same as those previously described. The mean of the two experiments gives for the atomic weight $\text{Co} = 59.045$. The cobaltous chloride was prepared by decomposing purpureo-cobalt chloride at 200° and eliminating the remaining ammonium chloride by heating in a current of nitrogen and hydrogen chloride. The cobaltous chloride was found to contain small quantities of ammonium chloride, alkali salts, and silica.

Cobaltous oxide is prepared by precipitating a solution of pure cobalt in nitric acid with ammonia, and after heating the precipitate over a spirit burner, decomposing the resulting black oxide at a red heat in a vacuum. The reduction of the cobaltous oxide by means of hydrogen gave for the atomic weight $\text{Co} = 58.954$ (mean of three experiments). An examination of the cobaltous oxide shows that it contains a small quantity of a higher oxide; also, by heating the oxide in a vacuum at 800° , a partial reduction takes place into metal and oxygen, and since a perfectly constant oxide could not be obtained, the authors have abandoned the experiments.

The results of all the experiments show that the atomic weight of cobalt lies between 58.93 and 59.06 and the most probable value is $\text{Co} = 58.995$ when $\text{O} = 16$.
E. C. R.

Occlusion of Hydrogen by Cobalt and other Metals. By GREGORY P. BAXTER (*Amer. Chem. J.*, 1899, 22, 351—364).—Although cobalt in the form of ingots, which therefore presents a minimum amount of surface, is known to occlude practically no hydrogen, it is

found that when reduced from the oxide, and therefore in a very finely divided condition, it occludes relatively large amounts of this gas. Electrolytic foil, which although somewhat porous lies between the two modifications in relative surface, falls between them also in its occluding power. The volume of occluded hydrogen varies, in the case of metal reduced from the oxide, with its purity and the temperature of reduction; it is remarkable that the metal reduced from cobalt bromide occludes practically no hydrogen; this appears to be due to its being deposited in a more compact form than that reduced from the oxide, as the presence of sodium bromide has no perceptible effect on the amount of occluded gas. Since the occlusion of hydrogen progresses very slowly at the ordinary temperature and is practically negligible at the temperature of reduction ($400-500^{\circ}$), it must be a maximum at some intermediate temperature; the time during which the metal is in contact with hydrogen determines largely the amount of gas taken up. Although practically none of the hydrogen occluded is given off in a vacuum at the ordinary temperature, yet on heating in a vacuum nearly the whole is evolved.

The occlusion of hydrogen by nickel appears to be governed by similar conditions to those dealt with in the case of cobalt; with pure copper and silver, the occlusion is practically *nil*. W. A. D.

Chromyl Chloride, Chlorochromic Acid, and Aminochromic Acid. By RICHARD JOS. MEYER and HANS BEST (*Zeit. anorg. Chem.*, 1899, 22, 192—199).—Chromyl chloride is obtained by the action of hydrogen chloride on a solution of chromic acid in acetic acid, but cannot be separated from the acetic acid solution. When pyridine, dissolved in acetic acid, is added to the solution, chlorine is evolved, and the *pyridine* salt of hexachlorotrichromyl chloride, $\text{Cr}_3\text{O}_3\text{Cl}_6 \cdot 3\text{PyHCl}$, is obtained, which crystallises in brownish-gold leaflets. The same salt is also obtained by adding pyridine hydrochloride to a solution of pure chromyl chloride in acetic acid.

Pyridine and quinoline, when added to a solution of potassium chlorochromate in acetic acid, yield pyridine and quinoline chlorochromates respectively, which separate in yellowish-red crystals, are stable, and can be recrystallised from dilute hydrochloric acid.

No evidence of the formation of aminochromic acid was obtained by the action of ammonia on a solution of potassium chlorochromate in dry acetone. E. C. R.

Recovery of Chromic Acid from Chromium Residues. By FRIEDRICH REGELSBERGER (*Zeit. angew. Chem.*, 1899, 1123—1128).—Various methods have been suggested for recovering chromic acid (compare Häussermann, *Dingl.*, 288, 163; Lorenz, *Abstr.*, 1896, ii, 265; Heibling, French Pat. 275274; Fitzgerald, Eng. Pat. 1896, 5542; Dercum, Eng. Pat. 1898, 3801; Meister, Lucius, and Brüning, German Pat. 103860). Two different electrolytic methods are described in the paper. The one consists in oxidation in alkaline solution: a current is passed through a saturated solution of an alkaline chloride containing an amount of chromic oxide or chromium salt equivalent to the current in unit time. When potassium chloride is employed, potassium dichromate crystallises from the hot solution

after some time, and chlorine is liberated. The metal vessel in which the electrolysis was conducted served as the cathode, and platinum gauze as the anode, and, to ensure complete admixture, air was blown through. The method may be of practical use when the chromium liquors contain considerable amounts of organic matter, or when solid chromium residues have to be dealt with.

The second method consists in the use of lead anodes in acid solution, either with or without a diaphragm; the lead is first converted into peroxide, which then oxidises the chromium compounds. The electrolysis proceeds best in hot solution, and almost any metal may be employed as cathode. Iron salts must not be present in the liquid.

J. J. S.

Preparation of Molybdenum and Uranium with the Aid of Liquid Air. By ALFRED STAVENHAGEN (*Ber.*, 1899, 32, 3065. Compare next abstract but one).—The yield of molybdenum from a mixture of molybdic acid, aluminium, and liquid air is poor, owing to the volatility of molybdic oxide. A mixture of uranic acid and aluminium explodes with great difficulty, but when liquid air is added, the reaction is very violent, and a thoroughly fused uranium regulus is obtained.

G. T. M.

Molybdenum Dioxide. By MARCEL GUICHARD (*Compt. rend.*, 1899, 129, 722—725).—Various oxides of molybdenum, intermediate in composition between MoO_2 and MoO_3 , have been described by former observers as being produced by heating molybdenum trioxide with ammonium molybdate and by the electrolysis of fused molybdenum trioxide. Both these reactions have been studied by the author, who finds that the sole product, after excess of molybdenum trioxide has been removed by successive washing with soda and hydrochloric acid, is in each case molybdenum dioxide, which was obtained in a pure, crystalline state.

N. L.

Preparation of Tungsten with the Aid of Liquid Air. By ALFRED STAVENHAGEN (*Ber.*, 1899, 32, 3064—3065).—The addition of liquid air to the mixture of aluminium and tungstic acid employed in the preparation of tungsten (*Abstr.*, 1899, ii, 489), produces, on explosion, so great a rise of temperature that a completely fused regulus of tungsten is obtained which contains only traces of aluminium. The author was unable to obtain the element by Hallepeau's electrolytic method (*Abstr.*, 1899, ii, 158). When molten lithium paratungstate is electrolysed with a current of 3.5 ampères and an E.M.F. of 12 volts, bluish-black crystals of lithium-tungsten bronze are produced.

G. T. M.

Tungsten. By EDGAR F. SMITH (*J. Amer. Chem. Soc.*, 1899, 21, 1007—1008).—An introductory paper, referring to those treated in the following abstracts and in this vol., i, 76, 89.

J. J. S.

Atomic Weight of Tungsten. By EDGAR F. SMITH and WILLET L. HARDIN (*J. Amer. Chem. Soc.*, 1899, 21, 1017—1027. Compare *Abstr.*, 1898, ii, 336).—Recent experiments prove that practically no hydrogen is occluded when metallic tungsten is allowed to cool in an atmosphere of this gas (compare Waddell, *Abstr.*, 1887, 112; Derenbach,

Inaug. Diss. Würzburg, 1892). It has been proved that tungsten trioxide exists in two varieties, crystalline and amorphous. These differ in specific gravity and also in their solubility in sulphur monochloride; they may be converted into one another. If the insoluble oxide is converted into ammonium tungstate and then ignited, the oxide which is formed dissolves in sulphur chloride at 145° , and when the metal obtained from the oxychloride is heated in a current of oxygen, the oxide formed is insoluble in sulphur chloride at 145° .

The authors conclude that, so far, there is no trustworthy method for the determination of the atomic weight of tungsten. The methods they have employed are (1) heating pure tungsten in air or in pure oxygen; (2) precipitating metallic silver from silver nitrate solution by the aid of metallic tungsten (compare Smith, *Abstr.*, 1893, ii, 170); (3) estimating the water of crystallisation in barium metatungstate (compare Scheibler, *J. prakt. Chem.*, 1861, 83, 324). In no case were concordant results obtained.

J. J. S.

Action of Sulphur Monochloride on Tungsten Trioxide. By EDGAR F. SMITH and HERMANN FLECK (*J. Amer. Chem. Soc.*, 1899, 21, 1008—1013).—When tungsten trioxide, the dioxide, or the mineral wolframite or scheelite is heated with sulphur monochloride, a red solution of tungsten oxychloride, $WOCl_4$, is obtained, together with a small amount of a brown, insoluble substance. The trioxide obtained by heating ammonium tungstate, or the trioxide which has been heated for some time in the air, is not completely acted on by sulphur chloride, whereas the trioxide obtained by heating the oxychloride is practically all dissolved by it. This difference is not due to the presence of a nitride or oxynitride. Tungsten itself is not acted on by pure sulphur monochloride, but if free chlorine is present, tungsten hexachloride is formed.

J. J. S.

Rays Emitted by Uranium and Thorium Compounds. By SKŁODOWSKA CURIE (*Compt. rend.*, 1898, 126, 1101—1103).—The electrical conductivity of air, when induced by the Becquerel rays emitted by uranium compounds, varies directly with the amount of this element present in the active substance. All uranium compounds are active, and the metal itself more so than any of its derivatives, except pitchblende and native chalcocite (copper uranylphosphate); the latter substance, however, when prepared artificially, is less active than the metal; these results seem to indicate that the two minerals contain an element far more active than uranium. Thorium compounds are very active, the action of thoria being more pronounced than that of metallic uranium; cerium, niobium, and tantalum compounds are slightly active. Yellow phosphorus is extremely active, but its action is probably of a nature different from that of uranium and thorium; in the allotropic form and in the phosphates, it is quite inert; the compounds of all other elements do not appreciably influence the electrical conductivity of air. The effects produced by the rays vary directly with the thickness of the layer of active substance; the rays traverse thin sheets of glass, ebonite, paper, and the metals. The rays emitted by thoria are more penetrating than those from uranium, and the penetrative power is augmented by increasing the layer of the oxide.

Distinct photographic impressions are obtained in the case of uranium, uranous oxide, pitchblende, chalcocite, and thoria, but those produced by thorium sulphate and potassium fluoroxytantalate are very faint. When uranium and thorium compounds are subjected to the influence of Röntgen rays, they emit secondary rays, which produce a more intense effect than those emitted by lead under similar conditions.

G. T. M.

New Radio-active Substance contained in Pitchblende. By P. CURIE and SKŁODOWSKA CURIE (*Compt. rend.*, 1898, 127, 175—178. Compare preceding abstract).—A specimen of pitchblende, having $2\frac{1}{2}$ times the emissive power of uranium, was examined chemically with a view of isolating the radio-active principle which produces the abnormal activity. The mineral was dissolved in acids and treated with hydrogen sulphide, the thorium and uranium remain in solution, whilst the active substance is precipitated with the sulphides insoluble in ammonium sulphide; after separating these in the usual manner, it is found that the substance in question remains with the bismuth.

When the sulphides are treated with nitric acid, the less active portion dissolves more readily; and when the solution of the nitrates is diluted with water the more active portion is first precipitated; the progress of the separation is controlled by determining the electrical conductivity of air induced by the various fractions. An extremely active product can be isolated from pitchblende by sublimation, and when the sulphides of bismuth and the active substance are heated in a vacuum at 700° , a sublimate is obtained, the activity of which is 400 times that of uranium. It is believed that the extremely active substance obtained from pitchblende contains an unknown metal to which the name *polonium* is given. Spectroscopic examination of the substance, however, has not revealed the existence of any characteristic lines indicating the presence of a new element.

G. T. M.

An extremely Radio-active Substance contained in Pitchblende. By P. CURIE, SKŁODOWSKA CURIE, and GUSTAVE BÉMONT (*Compt. rend.*, 1898, 127, 1215—1217. Compare preceding abstracts).—In the course of their researches on radio-active substances, the authors have obtained a product having all the properties of barium chloride, and, in fact, consisting mainly of this compound, but differing from the ordinary chloride in being extremely active. By repeated fractional precipitation of the active chloride from its aqueous solution by alcohol, a product is obtained which is 900 times more active than uranium. Ordinary barium salts are never radio-active, and, moreover, spectroscopic examination of the active substance has revealed the presence of a well-defined line not belonging to any known element (compare following abstract); the distinctness of the line increases with the radio-activity of the fraction under inspection. For these reasons, it is supposed that the active barium chloride contains another radio-active element for which the name *radium* is proposed. The atomic weight of barium in the active salt is not markedly different from that of the element in its inactive compounds.

The compounds of uranium, thorium, polonium, and radium all give photographic effects on sensitive plates, and in this respect

polonium and radium are far more active than the other two; the rays emitted by the new elements render barium platinoeyanide fluorescent, but the effect is less marked than with Röntgen rays.

G. T. M.

Spectrum of a Radio-active Substance [in Barium Chloride]. By EUGÈNE DEMARÇAY (*Compt. rend.*, 1898, 127, 1218. Compare preceding abstract).—The spectrum of the radio-active barium chloride, together with distinct indications of barium and faint lines due to lead, calcium, and platinum (from electrodes), contains a well-defined line of wave-length 3814·8 (Rowland's scale) which appears between the platinum lines 3819·9 and 3801·5; this line has not been noticed in the spectra of any of the known elements.

G. T. M.

Spectrum of Radium. By EUGÈNE DEMARÇAY (*Compt. rend.*, 1899, 129, 716—717).—The following lines characteristic of radium were obtained from the photographed spectrum of a specimen of barium chloride containing that element. The numbers 1 to 16 indicate the order of intensity. λ , 4826·3, (10); 4726·9, (5); 4699·8, (3); 4692·1, (7); 4683·0, (14); 4641·9, (4); 4627·4, (4), the centre of a nebulous band; 4600·3, (3); 4533·5, (9); 4458·0, (3), the centre of a nebulous band; 4436·1, (8); 4364·2, (3); 4340·6, (12); 3814·7, (16); 3649·6, (12). A number of feeble lines of uncertain origin were also observed.

N. L.

Atomic Weight of the Metal in Radio-active Barium Chloride. By SKŁODOWSKA CURIE (*Compt. rend.*, 1899, 129, 760—762).—Radio-active barium chloride obtained from a large quantity of uranium residues was fractionally crystallised, and the radio-active constituent was found to accumulate in the less soluble portions; when the latter were dissolved in water and fractionally precipitated by alcohol, the active substance was concentrated in the first precipitates. The atomic weight of the radio-active barium increases with the intensity of the radiation; with an intensity 3000 times as great as that of uranium, the atomic weight is 140·0; 4700 times as great, 140·9, and 7500 as great, 145·8. The radio-activity of the crystallised or precipitated compounds increases in a marked manner for several weeks after their preparation, but eventually attains a limiting value which may be five or six times as great as the value immediately after their preparation (compare Giesel, *Ann. Phys. Chem.*, 1899, [ii], 69, 91).

C. H. B.

Enantiotropy of Tin. By ERNST COHEN and C. VAN EYCK (*Proc. K. Akad. Wetensch. Amsterdam*, 1899, 2, 77).—It is well known that at low temperatures tin becomes converted into a grey powder, but the change has been but little investigated, and various reasons have been assigned for it. The authors find that at -83° the change occurred in about 24 hours, and the reverse transition could not be observed below 30° . At temperatures between these limits, the velocity of the change becomes so small as to be incapable of measurement. By the addition of a few drops of a 10 per cent. solution of ammonium stannic chloride, however, the reaction is considerably accelerated, and dilatometric observations employing this liquid for measurement purposes indicated

a temperature of between 10° and 20° for the transition. Determinations of the E.M.F. of the cell: white tin/10 per cent ammonium stannic chloride/grey tin, gave 20° for the temperature of transition. It hence appears that all tin exists, save in exceptionally warm weather, in the metastable condition. L. M. J.

Thio- and Seleno-antimonites. By ISIDORE POUGET (*Ann. Chim. Phys.*, 1899, [vii], 18, 508—571. Compare Abstr., 1897, ii, 499).—The following salts are described for the first time. *Lithium orthothioantimonite*, $\text{Li}_3\text{SbS}_3 + 3\text{H}_2\text{O}$, forms white, deliquescent crystals; the *para-salt* $\text{Li}_2\text{Sb}_4\text{S}_7 + 3\text{H}_2\text{O}$, is a dark red, gelatinous precipitate which has not been obtained crystalline.

Ammonium orthothioantimonite, $(\text{NH}_4)_3\text{SbS}_3$, is precipitated as a white, crystalline powder on adding alcohol to the mother liquor from the meta-salt; it readily decomposes and is only stable in the presence of ammonium sulphide.

Barium metathioantimonite, $\text{Ba}(\text{SbS}_2)_2 + 4\frac{1}{2}\text{H}_2\text{O}$, is an amorphous, brown precipitate.

Triargentic thioantimonite, Ag_3SbS_3 , is obtained as an amorphous, black precipitate by the addition of silver nitrate to a dilute solution of potassium orthothioantimonite; the double salt, Ag_2KSbS_3 , is a yellow, crystalline precipitate produced by the action of silver nitrate on concentrated solutions of the potassium ortho- or pyro-salt (Sommerlad, Abstr., 1897, ii, 500). A series of double salts of the formula RAg_2SbS_3 is obtained from sodium, lithium, and ammonium thioantimonites; these compounds are all decomposed by water into triargentic thioantimonite and the corresponding alkali salt.

Zinc orthothioantimonite, $\text{Zn}_3(\text{SbS}_3)_2$, forms a yellow, crystalline precipitate, produced by the action of zinc salts on dilute solutions of potassium thioantimonite; the *double salt*, ZnKSbS_3 , is obtained when concentrated solutions are employed.

The corresponding *manganese salts*, $\text{Mn}_3(\text{SbS}_3)_2$ and MnKSbS_3 , are produced in a similar manner; they form pale red, crystalline precipitates.

The *lead salts*, $\text{Pb}_3(\text{SbS}_3)_2$ and PbKSbS_3 , are brown precipitates. The reaction between potassium orthothioantimonite and cadmium, nickel, cobalt, and ferrous salts, follows the same course as in the preceding examples, but the products are very unstable.

Cuprous potassium orthothioantimonite, $\text{Cu}_2\text{KSbS}_3 + 3\text{H}_2\text{O}$, is a yellow, crystalline precipitate obtained by treating a cupric salt with excess of a concentrated solution of potassium orthothioantimonite; *cuprous orthoantimonite*, Cu_3SbS_3 , is produced by treating the preceding double salt with water; it is a red, crystalline precipitate. A black precipitate of *cupric thioantimonite* is formed when cupric salts are treated with a dilute solution of potassium orthothioantimonite; if, however, the latter reagent is in excess, it gradually reduces the cupric salt and the precipitate then consists of a mixture of this compound with the cuprous salt.

When mercurous salts are added to solutions of the alkali orthothioantimonites, the yellow precipitate at first produced is rapidly converted into a black deposit of mercury; mercurous salts react in a

similar manner. Gold chloride, when mixed with a concentrated solution of thioantimonite, produces a brown precipitate; this redissolves on agitation, and the solution, when warmed, deposits metallic gold.

Potassium orthoselenoantimonite, K_3SbSe_3 , is obtained in the form of orange crystals on evaporating a solution of antimony selenide in potassium selenide in a current of hydrogen; the salt is extremely unstable and its solution rapidly deposits selenium. The *para*-salt $K_2Sb_4Se_7 + 3H_2O$, separates as a gelatinous, brown precipitate on cooling a saturated solution of its generators.

Sodium orthoselenoantimonite, $Na_3SbSe_3 + 9H_2O$, crystallises in yellow needles from a solution of antimony selenide in sodium selenide; it is even more oxidisable than its potassium analogue, and its solution deposits red, tetrahedric crystals of sodium selenoantimonate, $Na_3SbSe_4 + 9H_2O$.

By the joint action of selenium and antimony dissolved in potassium sulphide, the mixed *salt*, $K_{10}Sb_4S_5Se_6 + 4H_2O$, is produced; it separates from the concentrated solution in small, yellow crystals. When a solution of sodium selenide is employed as the medium, two compounds are produced; the less soluble is a complex *salt* having the composition $Na_3SbS_{1.5}Se_{2.5} + 9H_2O$, which corresponds with the thioantimonate, $Na_3SbS_4 + 9H_2O$; the more soluble *salt*, $Na_3SbS_{1.5}Se_{1.5} + 9H_2O$, forms yellow needles and is analogous to the orthoantimonite, $Na_3SbS_3 + 9H_2O$.

Tellurium derivatives, analogous to the preceding compounds, could not be prepared; antimony telluride does not dissolve in a hot solution of potassium telluride, K_2Te , or potassium hydrotelluride, $KHTe$, and tellurium itself is insoluble in alkali sulphides. G. T. M.

Derivatives and Atomic Weight of Palladium. By WILLETT LEPLEY HARDIN (*J. Amer. Chem. Soc.*, 1899, 21, 943—955. Compare Rosenheim and Maass, *Abstr.*, 1899, i, 163).—Palladobis-phenylammonium chloride, $Pd(NH_2PhCl)_2$, is obtained as a voluminous yellow precipitate when a slight excess of aniline is added to a hydrochloric acid solution of palladious chloride, it is insoluble in hydrochloric acid, but dissolves in ammonium hydroxide solution; the *bromide*, $Pd(NH_2PhBr)_2$, resembles the chloride. *Palladodiquinolinium chloride*, $Pd(C_9NH_7Cl)_2$, the corresponding *bromide* and *palladodipiperidium chloride*, $Pd(C_5NH_{11}Cl)_2$, all form pale yellow precipitates. They are not acted on by hydrogen at the ordinary temperature, but are readily reduced to metallic palladium when heated in hydrogen and the product allowed to cool in a current of air. A compound, $PdCl_2 \cdot 2NH_3 \cdot Et \cdot 2HCl$, crystallising in brownish-red scales has also been prepared.

The atomic weight of palladium has been determined by various authorities (Berzelius, 1828; Keiser, *Abstr.*, 1890, 17; Keller and Smith, *ibid.*, 1893, ii, 73; Bailey and Lamb, *Trans.*, 1892, 61, 745; Joly and Leidie, *Abstr.*, 1893, ii, 284; Keiser and Breed, *ibid.*, 1894, ii, 141) and has now been determined by analysing diphenylpalladodiammonium chloride (seven experiments) and bromide (five experiments), and also ammonium palladium bromide (four experi-

ments), all of which were prepared from carefully purified palladium. The mean result obtained was 107.014 ($O = 16$), which is somewhat above that given by other authorities. J. J. S.

Mineralogical Chemistry.

Libollite. By JACINTO PEDRO GOMES (*Comm. Direc. Trabalhos Geol. Portugal*, 1898, 3, 244—250, 290—291).—Libollite is the name given to an asphalt resembling albertite which is found near Libollo, province of Angola, in Portuguese West Africa. Analysis gave :

C.	H.	O.	N.	Ash.	Sp. gr.
74.74	7.83	8.80	1.71	6.92	1.1

L. J. S.

Limonite Pseudomorphs from Dutch Guiana. By ROSSITER W. RAYMOND (*Trans. Amer. Inst. Mining Eng.*, 1899, 28, 235—239).—The auriferous alluvial deposits in the Saramacca district of Dutch Guiana contain cubes of limonite pseudomorphous after pyrites; these are sometimes hollow and are partly filled with a reddish powder. Analyses by A. R. Ledoux of the outer light red crust gave I, and of the interior darker red material gave II.

	Fe ₂ O ₃ .	Al ₂ O ₃ .	SiO ₂ .	H ₂ O.	Total.
I.	42.90	17.70	30.44	5.90	96.94
II.	87.94	0.90	2.34	7.50	98.68

A small amount of gold is present in II, but not in I. L. J. S.

Chromite from Newfoundland. By GEORGE W. MAYNARD (*Trans. Amer. Inst. Mining Eng.*, 1898, 27, 283—288).—Deposits of chromite are found in serpentine at Port-au-Port Bay, on the west coast of Newfoundland. Analysis by E. Waller of a selected sample of the ore gave :

Cr ₂ O ₃ .	FeO.	MgO.	Al ₂ O ₃ .	SiO ₂ .	Total.
49.23	17.21	18.66	7.50	6.51	99.11

Also traces of calcium, vanadium, copper and manganese.

L. J. S.

Occurrence of Nickel in Silesia. By O. H. ASCHERMANN (*Zeit. Kryst. Min.*, 1899, 32, 106; from *Inaug. Diss. Breslau*, 1897, 43 pp.).—Nickel occurs at Frankenstein, Silesia, as silicates in a red decomposition product of serpentine (*Abstr.*, 1895, ii, 514). The unaltered serpentine contains, according to two determinations, 0.0866 and 0.148 per cent. of nickel.

L. J. S.

Leverrierite. By PIERRE TERMIER (*Bull. Soc. franç. Min.*, 1899, 22, 27—31).—Previous analyses of this mineral are unsatisfactory, owing to the presence of admixed quartz and clay. A new analysis made on more pure material from Rochebelle, Gard, gave the following results. Sp. gr. 2.598.

SiO ₂ .	Al ₂ O ₃ .	Fe ₂ O ₃ .	MgO.	CaO.	K ₂ O.	Loss on ignition.	Total.
49.90	37.02	3.65	0.30	trace	1.13	8.65	100.65

The material analysed was dried at 110°. The loss on ignition is mainly water with a very little carbonaceous matter. The colourless crystals become white at 500°. This analysis agrees approximately with the formula $(\text{H}, \text{K})_2\text{O} \cdot (\text{Al}, \text{Fe})_2\text{O}_3 \cdot 2\text{SiO}_2$. The mineral therefore differs from kaolinite $(2\text{H}_2\text{O}, \text{Al}_2\text{O}_3, 2\text{SiO}_2)$, and resembles muscovite, but has water largely replacing potash.

Optical determinations are also given.

L. J. S.

Minerals of Japan. By KOTORA JIMBŌ (*J. Sci. Coll. Imp. Univ. Tokyo*, 1899, 11, 213—281).—A description, dealing mainly with occurrences, is given of 128 mineral species found in Japan. Some of the information has been previously published in Japanese journals. Analyses are given of the following.

Topaz. Good crystals of topaz are found at Takayama, &c., in province Mino, and at Tanokamiyama in province Ōmi. The crystals from Ōmi are usually brownish and occur with flesh-red felspar; analyses by Takayama gave the results under I and II.

Olivine in brown crystals occurs with crystals of augite in a basalt at Nishinotake in Hizen; analysis III by Kondō.

	SiO ₂ .	Al ₂ O ₃	MgO.	FeO.	CaO.	F.	Total.
I.	31.30	56.72	—	—	—	18.36	106.38
II.	31.95	56.59	—	—	—	18.01	106.55
III.	38.74	—	43.53	16.60	trace	—	98.87

Axinite occurs in the copper mine at Ōkuradani, Obira, province Bungo, associated with hedenbergite, garnet, copper pyrites, mispickel, pyrrhotite, fluor, &c. The crystals are dark brown to dark violet, and are somewhat prismatic in habit instead of the more usual sharp-edged or thin-tabular habit characteristic of the mineral. Analysis IV, by Kajiura.

	SiO ₂ .	Al ₂ O ₃ .	Fe ₂ O ₃ .	Mn ₂ O ₃ .	B ₂ O ₃ .	CaO.	MgO.	Na ₂ O.	K ₂ O.	H ₂ O.	Total.
IV.	41.87	19.25	11.79	5.62	1.59	17.75	trace	1.79	trace	0.87	100.53

Biotite? The pegmatite at Tanokamiyama in Ōmi contains several varieties of mica. Analysis V, by Kodera, is of dark green plates of biotite (?) which is nearly optically uniaxial.

Zinnwaldite (?), from the same place, is reddish-brown to nearly colourless; the plane of the optic axes is parallel to the plane of symmetry, and the axial angle is large. Analysis VI by Kodera.

A dirty, dark brown mica from Kai gave VII, by Hida.

	SiO ₂ .	TiO ₂ .	Al ₂ O ₃ .	Fe ₂ O ₃ .	FeO.	MnO.	CaO.	MgO.	K ₂ O.	Na ₂ O.	H ₂ O.	F.	Total.
V.	35.87	0.35	22.69	20.90	—	5.65	—	0.32	6.70	2.52	1.00	3.19	99.19
VI.	46.13	2.77	17.03	4.64	—	6.27	—	0.43	10.09	4.12	2.31	6.89	100.68
VII.	38.45	—	15.53	22.73	1.71	—	2.22	7.85	2.25	2.16	7.20	—	100.10

Hedenbergite occurs as large crystals in biotite-hornfels associated with axinite, &c. (*ante*) at Ōkuradani. Analysis VIII:

	SiO ₂ .	FeO.	MnO.	CaO.	MgO.	K ₂ O.	Na ₂ O.	H ₂ O.	Total.
VIII.	47.13	24.46	0.73	23.23	2.40	0.13	0.98	1.48	100.54

Orthoclase and *Microcline*. Several types of potash feldspars occur in druses in pegmatite at Tanokamiyama, Ōmi. Analysis IX of white, translucent crystals, usually twinned, and up to 20 cm. long. Analysis X, reddish-white to flesh-red crystals occurring with topaz; XI and XII, of glassy crystals mostly twinned (Analysis IX—XII by Kōdera).

	SiO ₂ .	Al ₂ O ₃ .	Fe ₂ O ₃ .	CaO.	MgO.	K ₂ O.	Na ₂ O.	Total.
IX.	64.78	17.86	1.46	0.14	0.11	12.87	2.25	99.47
X.	64.62	21.00	0.33	0.20	0.09	12.22	2.41	100.87
XI.	63.77	19.52	1.39	—	0.08	13.70	1.84	100.30
XII.	64.98	22.17	0.32	—	0.86	10.59	0.60	99.52

Sphene. Small yellow crystals in diorite at Kamioka in Hida gave analysis XIII, by Yoshida.

Heulandite. White, translucent crystals showing optical anomalies, from Ohara, gave analysis XIV, by Shinowara.

	SiO ₂ .	TiO ₂ .	Al ₂ O ₃ .	Fe ₂ O ₃ .	CaO.	MgO.	H ₂ O.	Total.
XIII.	30.81	40.21	0.61	0.51	26.42	1.21	—	99.77
XIV.	58.4	—	14.4	—	12.2	—	14.9	99.9

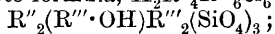
L. J. S.

New Minerals from Franklin, New Jersey. By SAMUEL L. PENFIELD and CHARLES H. WARREN (*Amer. J. Sci.*, 1899, [iv], 8, 339—353).—The new minerals were found in the zinc mines at Franklin, in association with native copper and lead (Abstr., 1898, ii, 602), clinohedrite (Abstr., 1898, ii, 607), rœblingite (Abstr., 1897, ii, 563), axinite, willemite, datolite, garnet, phlogopite, &c. They are probably of metamorphic (pneumatolitic) origin.

Hancockite. This occurs as brownish-red, cellular masses of minute, lath-shaped crystals, which are monoclinic, and have nearly the same habit and angles as epidote. Single crystals are yellowish-brown with a vitreous lustre, and are pleochroic. Sp. gr. 4.030. Analysis by Warren gave :

SiO ₂ .	Al ₂ O ₃ .	Fe ₂ O ₃ .	Mn ₂ O ₃ .	PbO.	MnO.	MgO.	CaO.
30.99	17.89	12.33	1.38	18.53	2.12	0.52	11.50
SiO.				H ₂ O.	Total.		
3.89				1.62	100.77		

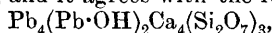
This gives the epidote formula, $H_2R''_4R'''_6Si_6O_{26}$, or



but the mineral differs from epidote in containing lead and strontium isomorphous with calcium. Like epidote, the mineral is decomposed by hydrochloric acid only after ignition.

Glaucokroite. This occurs embedded in nasonite as columnar, orthorhombic crystals of a bluish-green colour. Twins are sometimes present with individuals intercrossing at angles of about 60°. The parameters are approximately $a:b:c=0.440:1:0.566$; these ratios, as well as the optical characters, indicate that the mineral belongs to the olivine group. Sp. gr. 3.407. Analysis I, by Warren, gives the formula $CaMnSiO_4$, showing that the mineral takes a place next to monticellite ($CaMgSiO_4$).

Nasonite. This is white and massive, with a greasy to adamantine lustre. Thin sections under the microscope show the mineral to be crystalline and optically uniaxial; the system is probably tetragonal. Sp. gr. 5·425. After deducting 2·16 per cent. of clinohedrite ($\text{H}_2\text{CaZnSiO}_5$), analysis II (by Warren) gives the formula $\text{Pb}_6\text{Ca}_4\text{Cl}_2(\text{Si}_2\text{O}_7)_3 = \text{Pb}_4(\text{PbCl})_2\text{Ca}_4(\text{Si}_2\text{O}_7)_3$. This is closely related to the tetragonal ganomalite from Sweden, of which the formula is usually given as $\text{Pb}_3\text{Ca}_2\text{Si}_3\text{O}_{11} = \text{Pb}_4(\text{Pb}_2\text{O})'\text{Ca}_4(\text{Si}_2\text{O}_7)_3$. Lindström's analysis (1883) of ganomalite shows the presence of small quantities of water and chlorine, and it agrees with the formula



which is now proposed for ganomalite. Nasonite therefore differs from ganomalite in containing chlorine in place of hydroxyl.

The acid, $\text{H}_6\text{Si}_2\text{O}_7$, of which nasonite and ganomalite, as well as cordierite, barysilite ($\text{Pb}_3\text{Si}_2\text{O}_7$) and hardystonite (Abstr., 1899, ii, 435) are salts, is intermediate between ortho- and meta-silicic acids, or it may be considered as $2\text{Si}(\text{OH})_4 - \text{H}_2\text{O}$. For this acid, which is usually called diorthosilicic, the name *mesosilicic acid* is proposed.

Leucophaenite. This is of a purplish-red or raspberry colour; it has a crystalline structure, though the crystal system, probably monoclinic, could not be determined. Sp. gr. 3·848. Analysis III (also Na_2O , 0·39; K_2O , 0·24), by Warren, agrees with the formula $\text{H}_2\text{R}_7\text{Si}_3\text{O}_{14}$, or, as the water is not expelled below a red heat, $\text{R}_5(\text{R}\cdot\text{OH})_2(\text{SiO}_4)_3$. This represents a basic orthosilicate, and the mineral is therefore a manganese humite with hydroxyl in place of fluorine.

	SiO_2 .	PbO .	MnO .	ZnO .	MgO .	CaO .	FeO .	Cl .	H_2O .	Total.
I.	31·48	1·74	38·00	—	—	28·95	trace	—	—	100·17
II.	18·47	65·68	0·83	0·82	—	11·20	0·10	2·81	0·26	99·54
III.	26·36	—	60·63	3·87	0·21	5·67	trace	—	2·64	100·01

L. J. S.

Hydrated Aluminium Silicates and Clays. By KONSTANTIN D. GLINKA (*Zeit. Kryst. Min.*, 1899, 32, 79—81; from *Mém. Inst. agron. forest. à Novo-Alexandria* [*Gouv. Lublin*], 1899, 12, 41—84).—Various clays were found to contain quartz, orthoclase, muscovite, rutile, zircon, tourmaline and garnet, together with kaolin, bauxite and diaspore, but no zeolites. Quartz and aluminium hydroxides may occur together, and in this case their presence will not be indicated by a bulk analysis of the clay. Their presence is, however, indicated when the material, after ignition, is treated with a 33 per cent. solution of potassium hydroxide; under these circumstances, most of the silica, but very little of the alumina, goes into solution. Several other experiments of a similar nature were made on clays and various silicates, the object being to determine the constituent minerals of clays. L. J. S.

Stokesite, a New Mineral from Cornwall. By ARTHUR HUTCHINSON (*Phil. Mag.*, 1899, [v], 48, 480—481).—A preliminary notice is given of a new mineral, of which only a single crystal, about 10 mm. long, has been found. It is colourless and transparent. System, orthorhombic [$a:b:c = 0·3479:1:0·8117$]. Sp. gr. 3·185,

H = 6. The lustre is vitreous. Analysis gives the formula $\text{CaO}, \text{SnO}_2, 3\text{SiO}_2, 2\text{H}_2\text{O}$ (compare *Nature*, 1899, 61, 119). L. J. S.

Andesites from Maine. By HERBERT E. GREGORY (*Amer. J. Sci.*, 1899, [iv], 8, 359—369).—A description is given of the andesites of the Aroostook volcanic area of northern Maine. An analysis by Hillebrand is quoted. L. J. S.

Hot Sulphur Spring of Deutsch-Altenburg. By ERNEST LUDWIG and THEODOR PANZER (*Chem. Centr.*, 1899, ii, 402; from *Wien. klin. Wochens.*, 12, 708—710).—The hot sulphur spring of Deutsch-Altenburg belongs to the same type as the hot salt-sulphur springs of Aachen and of the Hercules bath in Mevania. It is a clear water, with a strong odour of hydrogen sulphide, and becomes turbid on keeping and deposits sulphur. It has a sp. gr. 1.00289 at 18.70° and contains traces of caesium, rubidium, titanic oxide and formic acid. A full analysis is given. E. W. W.

Origin of Graubünden Mineral Waters. By GUSTAV NUSSBERGER (*Jahresber. Naturforsch. Ges. Graubündens*, 1899, 42, 1—35. Compare *Abstr.*, 1897, ii, 569).—A detailed account is given of the mineral waters of the Canton Graubünden (= Grisons), Switzerland, and their origin discussed. Several analyses are quoted. L. J. S.

Mineral Waters of Lutraki, Greece. By ANASTASIOS K. DAMBERGIS (*Chem. Centr.*, 1899, ii, 568; from *Oesterr. Chem.-Zeit.*, 2, 437).—The mineral waters of Lutraki, on the north coast of the Gulf of Corinth, consist of three groups, which differ in temperature and quantity, but have an almost identical composition. The clear, odourless water has a sweet taste, with a somewhat saline after-taste, does not become turbid on exposure to air, and leaves no residue as it flows from the spring. The group containing the most dissolved matter contains 1.912 grams of dissolved substances per litre, has a temperature of 31°, and a sp. gr. 1.0018. An analysis is quoted. The springs belong to the class of alkaline calcareous hot springs. E. W. W.

The Water of Monsummano. By PIETRO ALBERTONI and GIUSTO CORONEDI (*Chem. Centr.*, 1899, ii, 591—592; from *Ann. Farm. Chim.*, 1899, 214—235).—The water of Monsummano has a temperature of 32° and a sp. gr. 1.000154, and 10,000 parts leave a residue of 13.012 dried at 180°. An analysis of the residue is quoted. In the original paper, the action of this water is discussed on the basis of the ion theory and clinical experiments on its therapeutic and physiological effects are also described. The small amount of calcium and magnesium salts present, and its power of dissolving uric acid, are remarkable. Uric acid dialyses much more readily into this water than into distilled water. E. W. W.

Physiological Chemistry.

Influence of Bile, of Acid, and of Alkalis on the Proteolytic Action of Pancreatic Juice. By BENJAMIN K. RACHFORD (*J. Physiol.*, 1899, 25, 165—178. Compare Abstr., 1899, ii, 567).—Experiments were made with the pancreatic juice (not extracts, as Chittenden used) and bile of the rabbit. These confirm the conclusion arrived at previously, although denied by Chittenden, that bile much favours the proteolytic action of the juice. Bile, however, retards the albuminous fermentations carried on by organised ferments. When pancreatic juice is added to fibrin half saturated with hydrochloric acid, it does as much work as on neutral fibrin. If the fibrin is nine-tenths saturated with the acid, proteolysis is retarded; this retardation also occurs in the presence of bile. Free hydrochloric acid greatly inhibits, but does not destroy, the proteolytic action, whilst sodium carbonate is favourable, especially in dilute solutions of pancreatic juice. The general conclusion is drawn that the conditions in the entire small intestine are favourable to the proteolytic activity of pancreatic juice.

W. D. H.

The Influence of Removal of Water on Metabolism and Circulation. By WALTHER STRAUB (*Zeit. Biol.*, 1899, 38, 537—566).—The effect of sodium chloride in producing a slight increase of proteid katabolism is attributed to its diuretic action, water being removed from the tissues. The present experiments on dogs were designed to test this theory by a removal of water from the food; this was found to increase proteid katabolism, but to have no influence on fat. The blood pressure is not altered, but the quantity of water lost by skin and lungs is slightly lessened.

W. D. H.

Influence of the Kind and Amount of Nutriment on Metabolism. By EDUARD PFLÜGER (*Pflüger's Archiv*, 1899, 77, 425—482).—The object of the paper is to show that proteid is the great source of energy; it increases metabolism, and raises the resistance and power of the animal; it does so by increasing the substance of the living cells, sometimes even doubling their weight. Fat and carbohydrate have no such power. Fat never arises from proteid in the animal body. Man cannot take all his nutriment in the form of proteid simply because of the limitation which exists in his digesting power.

W. D. H.

Metabolism of Nucleins. By T. H. MILROY and J. MALCOLM (*J. Physiol.*, 1899, 25, 105—130. Compare Abstr., 1899, ii, 479).—In a case of lymphatic leucocythæmia, the phosphoric oxide excreted was diminished both absolutely and relatively to the nitrogen excreted, whilst the excretion of uric acid and alloxuric bases was hardly affected. In a case of medullary leucocythæmia where the number of leucocytes was falling, the excretion of phosphoric oxide underwent no diminution, whilst the alloxuric excretion varied greatly. An investi-

gation of the characters of the granules in the colourless corpuscles of marrow and blood was carried out by micro-chemical means. Nucleic acid, and its principal decomposition products (thymic acid, adenine, guanine, cytosine) alter the staining affinities of oxyphil granules, making them finally basophil. The granules are nucleoproteid, and the action of the nucleic acid is to cause the cell to give up the albumin and leave a more acid residue, nuclein. The subsequent discharge of the residue leads to an increase of excreted phosphoric anhydride; this probably occurs in the body when nucleic acid is liberated. The granules readily undergo changes, and a study of them is important, for these affect the general metabolism.

W. D. H.

The Proteid-sparing Action of Alcohol. By RUDOLF ROSEMAN (Pflüger's Archiv, 1899, 77, 405—424).—Miura, Schmidt, and Schönesseffen found that alcohol has no proteid-sparing action. The present paper confirms this, and criticises Neumann's recent work, which appeared to show the contrary.

W. D. H.

Koppe's Theory of the Formation of Hydrochloric Acid in the Stomach. By JOHN A. WESENER (Pflüger's Archiv, 1899, 77, 483—484).—Koppe's theory of the formation of hydrochloric acid in the stomach is that ionisation of the sodium chloride in the stomach, and of the acid carbonates and phosphates in the blood, occurs, and that an exchange of the hydrogen ions in the blood, and sodium ions of the stomach then takes place. The following experiments show this cannot be the case, but that the acid is the result of cell activity. If the stomach is well washed out, and a 0·7 per cent. solution of sodium chloride introduced, there is no formation of free acid, but if the stomach be irritated by the rotation of a revolving sound in its interior, whether the sodium chloride solution be there or not, free hydrochloric acid appears, reaching a percentage of 0·1 in a few minutes.

W. D. H.

Origin of Fat from Proteid. By EDUARD PFLÜGER (Pflüger's Archiv, 1899, 77, 521—554).—Polemical. Pflüger is well known to be an unbeliever in Voit's doctrine that fat can originate from proteid in the body; his remarks here are mainly directed against Max Cremer, the latest exponent of Voit's theory.

W. D. H.

Phosphorus in Muscle. By J. J. R. MACLEOD (Zeit. physiol. Chem., 1899, 28, 535—558).—By muscular work, the organically united phosphorus in aqueous extracts of muscle is greatly diminished but the inorganic phosphates are increased. The lessening is due partly to a diminution of phosphorus in nucleon, but especially to that in organic phosphorus compounds other than nucleon.

W. D. H.

Sodium Chloride in Cartilage. By GUSTAV VON BUNGE (Zeit. physiol. Chem., 1899, 28, 452—458).—Cartilage, one of the oldest tissues, phylogenetically, is the richest of the tissues in sodium. A number of analyses of cartilage from mammals show that the sodium is most abundant in embryonic life, and least so in old animals. Com-

paring the cartilage of adult selachians with that of adult and embryonic mammals, the former is richest in sodium; doubtless the sodium is principally present as chloride.

W. D. H.

The Lactase of the Pancreas. By ERNST WEINLAND (*Zeit. Biol.* 1899, 38, 607—617).—In both young and adult dogs, the pancreas in virtue of a lactase converts lactose into dextrose and galactose, this power being increased by a milk diet. By prolonged boiling with citric acid, lactase is similarly acted on. There is no evidence of any intermediate substance between lactose and its hydrolytic products.

W. D. H.

The Retention of Phytosterol in the Animal Body after Feeding with Cotton-seed Oil. By C. VIRCHOW (*Chem. Centr.*, 1899, ii, 395; from *Zeit. Unters. Nahr. u. Genussmittl.*, 2, 559—575. Compare Abstr., 1899, ii, 689).—The results of experiments in which dogs and pigs were fed with cotton-seed oil showed that phytosterol did not pass into the fat, so that the presence of phytosterol in lard is important evidence of adulteration.

It was found that glycerides of hydroxy-fatty acids passed into the fatty tissues.

N. H. J. M.

Albumin in the Cell of the Queen Bee. By P. SÜSS (*Chem. Centr.*, 1899, ii, 560; from *Pharm. Centr.-H.*, 40, 458).—More than a gram of a yellowish-white, rather transparent mass with the appearance of salve was found on the floor of a queen bee cell and proved to be albumin. A. KLETT (*ibid.*, 502) points out that it has been long known that the cell of the queen bee contains albumin, and, indeed, differs from those of the working bees only in containing a larger proportion of it.

E. W. W.

Death Temperature of Marine Organisms. By HORACE M. VERNON (*J. Physiol.*, 1899, 25, 131—138).—In a number of marine animals belonging to various groups, the death temperature is generally a little higher than the paralysis temperature, and varies from 32.5° to 43.5°. Even among transparent pelagic animals, the differences are nearly as great. The differences can only be partly explained by the differences in the amount of solids in the tissues, hence protoplasm must vary chemically as well as physically. From observations on the death temperature of echinoid embryos, it is shown that it rises with the progress of development.

W. D. H.

Degradation of Caffeine in the Organism of the Dog. By MARTIN KRÜGER (*Ber.*, 1899, 32, 3336—3337. Compare Abstr., 1898, i, 699; 1899, ii, 233, and this vol., ii, 30 and 31).—Caffeine (1:4:6-trimethylxanthine) was given to a rabbit during 22 days in daily doses of 0.1 gram, the animal being fed on oatmeal and cabbage; the urine was found to contain paraxanthine (1:6-dimethylxanthine), heteroxanthine (1-methylxanthine), and 6-methylxanthine. In the systems of the rabbit and man, the methyl group in position 4 appears to be most labile, whilst in the dog the alkyl radicle in position 1 is most readily removed.

G. T. M.

Influence of Theine on the Excretion of Alkalis in the Urine. By K. KATSUYAMA, T. KUWAHARA, and K. SENO (*Zeit. physiol. Chem.*, 1899, 28, 587—594).—Experiments on rabbits show that the administration of theine increases the output of alkali in the urine; there is increase in sodium, but not in potassium. W. D. H.

Estimation of the Reducing Substances in Urine by Peške's Method. By A. GREGOR (*Chem. Centr.*, 1899, ii, 231; from *Centr. Krank. Harn. und Sexualorgane*, 10, 240).—The method of Peške (*Proc.*, 1895, 11, 43) for the estimation of dextrose is equally applicable to urine. The urine requires to be diluted. Normal urine shows a reducing power varying from 0.0825 to 0.347 per cent. It rises after a meal, more strongly after an amylaceous than after a flesh diet. It is constant during the night, having the same value (0.085 per cent.) as when fasting or employing a pure flesh diet. Excessive use of carbohydrates does not increase it; alcohol does so. It is lowered by hard, muscular work. M. J. S.

Relations between the Diuretic Effects and Osmotic Properties of Sugars. By E. HÉDON and J. ARROUS (*Compt. rend.*, 1899, 129, 778—781).—Sugars are toxic only in very large doses, and can be injected into the animal system without producing either immediate or subsequent accidents. The maximum diuretic effect is produced by a particular dose at a particular degree of concentration, which varies with different sugars. There is an approximately constant relation, the *diuretic coefficient D*, between the quantity of sugar solution injected and the volume of urine eliminated, but this coefficient varies with the concentration of the solution; with dextrose solution containing 25 per cent. it is 2.8, with 50 per cent. 4.8, and with 10 per cent. 1.0. The coefficient also varies with different sugars at the same degree of concentration; with dextrose at 25 per cent. it is 2.8; lævulose and galactose, 2.4; sucrose, 2.0; lactose and maltose, 2.2; raffinose, 0.9; arabinose, 3.4; erythritol, 4.0. It follows that the diuretic coefficients of these sugars vary inversely as their molecular weights, but directly as their osmotic pressures. Some sugars of the same molecular weights and osmotic pressures have not, however, exactly the same diuretic coefficients, but these differences are probably due to the different chemical functions of the sugars or to the fact that different proportions of them are consumed by the organism.

The toxic effect of the sugars generally follows the same order as their diuretic coefficients. The toxic dose is 30—35 grams per kilogram of body weight in the case of sucrose; 20—25 grams with dextrose; and 5 grams with arabinose and erythritol. C. H. B.

[Physiological Action of] Cyanotetramethylpyridone. By LUIGI SABBATANI (*Chem. Centr.*, 1899, ii, 528; from *Atti Real. Accad. Torino*, 34).—A 1 per cent. solution of the 3-cyano-1:2:3:4-tetramethylpyridone, prepared by Guareschi (*Atti Real. Accad. Torino*, 34), has an extremely bitter taste, which is similar to that of quinine and magnesium sulphate. With Bouchardat's reagent, this compound forms a reddish-brown precipitate which easily decomposes and with Nessler's reagent, even in very dilute solutions, it gives a lemon-yellow,

amorphous precipitate, but its presence in urine could not be detected by means of these reactions. Physiologically it proved to be very active, but comparatively harmless, its operation being of short duration and chiefly affecting the spinal marrow. When dropped into the eye, it induces myosis and subcutaneous injections have a purgative action. Dilute solutions of the pyridone cause more or less violent contraction of the muscles. E. W. W.

Physiological Action of Quinosol [*o*-Hydroxyquinoline-sulphonic Acid]. By CARL BRAHM (*Zeit. physiol. Chem.*, 1899, 28, 439—451).—The urine of animals (dogs and rabbits) which had been dosed with quinosol deposits crystals of *o*-hydroxyquinoline-glycuronic acid, $C_{15}H_{15}O_7N + 2H_2O$, and this does not show a definite melting point, but turns yellow at 102—105° and decomposes at 151°; it dissolves in 815 parts of water at 15°, but readily in hot water, the solution being strongly acid; it does not reduce Fehling's solution. The cadmium, strontium, barium, and potassium salts were prepared; an aqueous solution of the latter is laevorotatory $[\alpha]_D$ 83.83—76.59°. When boiled with dilute acids, the acid is resolved into *o*-hydroxyquinoline and glycuronic acid.

Nothing certain is known of the origin of glycuronic acid in the body; the administration of α -methylglucoside did not lead to its appearance in the urine. W. D. H.

Action of Lymphagogues on the Proteids of Blood and Lymph. By DMITRI J. TIMOFÉEFFSKY (*Zeit. Biol.*, 1899, 38, 618—651).—The percentage of globulin in relation to the total proteid is higher in normal blood than in lymph. Lymphagogues of Heidenhain's first kind increase this relationship, either only in the lymph (for example, with toxins and crayfish extract), or in both lymph and blood (as when peptone is used); this, however, lasts but a short time, the normal ratio being quickly re-established. The change in the proteids has no direct relation to the increase of lymph secretion, or the rise in the total proteids of the lymph. W. D. H.

Acute Alcoholism: Estimation of Alcohol in the Blood and the Tissues. By NESTOR GRÉHANT (*Compt. rend.*, 1899, 129, 746—748).—A 10 per cent. solution of alcohol was introduced into the stomach of dogs, in quantity corresponding with 5 c.c. of absolute alcohol per kilogram of body weight. After half-an-hour, 10 c.c. of arterial blood were withdrawn, and the alcohol in it estimated by distillation and titration with potassium dichromate, this operation being repeated every half-hour. After an hour and a half, the quantity of alcohol in the blood becomes constant and is 0.57 c.c. per 100 c.c. of blood. After four-and-a-half to five hours, the quantity of alcohol begins to be less and the animal slowly recovers. In the case of a dog killed by bleeding from the carotid artery, the following quantities of alcohol were found in the various tissues: brain, 0.41 c.c.; muscles, 0.33 c.c.; liver, 0.325 c.c.; kidneys, 0.39 c.c. per 100 grams of tissue in each case. C. H. B.

Effect of Poisons on the Eye-Muscles. By GUILLERY (*Pflüger's Archiv*, 1899, 77, 321—404).—A considerable number of measure-

ments of the movements of the ocular muscles were made under normal circumstances, and these were compared with others made under the influence of various poisons. Alcohol lessens the contractive-energy: this is principally manifested by the internal recti. The paralysing action of morphine falls also chiefly on the same muscles; the action on the external muscles begins later. The action of chloral hydrate on the eye-muscles is shown by quite small doses; the pupil is enlarged, and the near point is made more distant. Much larger doses of paraldehyde are necessary to produce corresponding effects; the action of sulphonal and trional is small but unmistakable. Cocaine has little or no action beyond that on the pupil. Chloroform is the most active of the inhalation poisons examined.

W. D. H.

Chemistry of Vegetable Physiology and Agriculture.

Do the Bacteria of Alinit assimilate Atmospheric Nitrogen?

By JULIUS STOKLASA (*Chem. Centr.*, 1899, ii, 132; from *Centr. Bakt. Parasit.*, II., 5, 350—354).—Whilst Lauck (*Chem. Centr.*, 1899, i, 443 and 858, and *Centr. Bakt. Parasit.*, II., 5, 20, 54, and 87) believes that the alinit bacteria are *Bacillus subtilis*, the author considers them to be *B. megatherium*. The two bacilli differ essentially; the former converts nitrates into nitrites, the latter into nitrites and ammonia.

In a mixture of xylose and galactose (3 : 1) with mineral matter and a little nitrogen (as peptone) the alinit bacteria develop quickly and fix free nitrogen. In presence of much combined nitrogen there is no fixation. In the same mixture, *B. subtilis* grows less and there is only a slight fixation of free nitrogen. N. H. J. M.

Influence of Organic Substances on the Work of Nitrifying Organisms. By SERGEI WINOGRADSKY and V. OMELIANSKY (*Chem. Centr.*, 1899, ii, 132—133, 217, and 264; from *Centr. Bakt. Parasit.*, II., 5, 329—343, 377—387, and 429—440).—Sodium carbonate is essential for the growth of nitric and nitrous organisms.

In the case of nitrate organisms, the oxidation of the nitrite and the growth of the microbe are inseparable. Peptone in excessive amount cannot alter the specific function of the microbe, but destroys or completely checks it under certain conditions. Addition of 0.025 per cent. of dextrose is favourable; the limit of favourable action is reached when 0.3 per cent. is present. Urea is without effect when the amount is only 0.05 per cent.; 0.5—0.8 per cent. hinders nitrification; asparagine (0.05 per cent.) is injurious, and glycerol behaves similarly.

Infusion of hay (14 per cent.) is beneficial; addition of urine (2 per cent.) resulted in the time required for oxidation being increased five times. Broth (8 per cent.) had no effect. Urea is without action

and it is to ammonia that the depressing effect of urine is attributed (compare Warrington, Trans., 1891, 521). Sodium acetate (2 per cent.) checked oxidation, whilst the butyrate had only a slight effect. Iron salts seem to assist the process.

The nitrite bacterium is much more sensitive to nitrogenous substances such as peptone and asparagine than the nitrate bacterium. The more complex, unstable, and, for most microbes, the more assimilable the substance, the more injurious is its effect on nitric organisms. The following arrangement of nitrogenous substances, according to their nutritive value, also corresponds with their anti-nitrifying effect: peptone, dextrose, asparagine, urea, acetates, and butyrates.

N. H. J. M.

Nitrification of Organic Nitrogen. By V. OMELIANSKI (*Chem. Centr.*, 1899, ii, 347—348; from *Centr. Bakt. Parasit.*, II., 5, 473—490).—Experiments with amides, proteids, urine, &c., showed that the nitrifying organisms are not able to attack organic nitrogen; the nitrogen must be first converted into ammonia.

A cultivation containing an ammonia microbe (*Bacillus ramosus*), a nitrite bacterium, and a nitrate bacterium converted organic nitrogen successively into ammonia, and nitrous and nitric acids. If the nitrite bacterium is omitted, only ammonia is formed, whilst if the nitrate bacterium is omitted, the change stops after production of nitrites.

N. H. J. M.

Micro-organisms observed in the Formation of Nitrates. By ALBERT STUTZER and R. HARTLEB (*Chem. Centr.*, 1899, ii, 448—449; from *Mitt. landw. Inst. k. Univ. Breslau*, Heft. 2).—A nitric organism, *Nitromicrobium germinans*, which is not a bacterium, was obtained from soil. It only oxidises nitrites to nitrates. As nitrogenous food, it can utilise ammonium compounds and nitrates as well as nitrites, but not complex compounds such as peptone and the constituents of broth. It utilises free carbon dioxide, but not carbonates, and it cannot assimilate the carbon compounds, such as sugars, usually employed for bacteria.

N. H. J. M.

Action of *Bacillus Coli* and *Bacillus D'Eberth* on Nitrates. By LÉON GRIMBERT (*Ann. de l'Inst. Pasteur*, 1899, 13, 67—76).—Nitrogen is not evolved, and only a trace of nitrite is formed, when *Bacillus coli* and *B. d'Eberth* are cultivated in a 1 per cent. peptone solution containing 1 per cent. of a nitrate. If, however, they are cultivated in peptonised broth containing a nitrate, then a part of this nitrate is decomposed, nitrogen and carbon dioxide are evolved, and a considerable amount of nitrite remains in solution. With *B. pyocyaneus* the whole of the gas evolved consists of nitrogen, no carbon dioxide being formed. Similar results are obtained with a peptone solution containing extract of meat and a nitrate. The evolution of nitrogen is no doubt due to a secondary reaction between the nitrous acid produced by the reduction of the nitrate by the bacillus, and the amino-nitrogen contained in the broth or extract, for the amount of nitrogen evolved is twice that corresponding with the amount of nitrate decomposed and half that corresponding with the aminic nitrogen

contained in the broth or extract. Peptone itself contains a small amount of aminic nitrogen, and it is therefore possible for *B. coli* and *B. d'Eberth* to evolve nitrogen from a 5 per cent. peptone solution, for the amount of peptone in the solution is sufficient to furnish the aminic nitrogen required. Nitrogen is evolved when *B. d'Escherich* and *B. d'Eberth* are cultivated in a peptone solution containing potassium nitrite.

H. R. LE S.

Denitrification. By KURT WOLFF (*Chem. Centr.*, 1899, ii, 133—134; from *Hygien. Rundsch.*, 9, 538—547).—Besides the eleven known denitrifying organisms, *Bacillus fluorescens liquefaciens* possesses this property, although it will not reduce nitrates in pure well or river water, or in milk.

As regards the question whether denitrifying organisms obtain oxygen wholly, or in part, from nitrates, it was found that the same amount of atmospheric oxygen was absorbed whether nitrates were present or not.

On inoculating peptone containing calcium nitrate with *B. fluorescens*, nitrogen was eliminated, nitrous anhydride being formed as an intermediate product. Calcium carbonate was formed; the liberation of nitrogen cannot therefore be the result of the interaction of nitrate and amino-compounds in acid solution, as Marpmann suggested (*Chem. Centr.*, 1899, i, 702, and *Centr. Bakt. Parasit.*, II, 5, 67). The fact that with abundant aëration nitrogen is not liberated may be due to the removal of most of the carbon dioxide. Other examples of microbes which only denitrify in presence of plenty of carbon dioxide are given.

Ordinary pressed yeast destroys nitrates completely both in broth containing sodium nitrate or with calcium nitrate. This is not a case of action of pure yeast, as numerous bacteria are present. Fermentation can take place without liberation of free nitrogen from the nitrate present.

N. H. J. M.

Which forms of Carbohydrates do Denitrification Bacteria require for their Vital Processes? By JULIUS STOKLASA (*Bied. Centr.*, 1899, 27, 707—708; from *Zeit. landw. Versuchswesen Oesterr.*, 1898, i, 371).—The activity of denitrification bacteria was found to be greatest in presence of xylose; arabinose is a less suitable food. Experiments were also made with pure dextrose, lævulose, galactose, and sucrose.

In experiments with *Bacillus denitrificans*, it was found that oats grew normally in presence of dextrose, whilst with xylose the yield was reduced to about one-fourth as compared with that of pots manured with nitrate and superphosphate. With arabinose, the results were similar to those obtained with glucose.

Bacillus megatherium and *B. mycoides* had no effect on the growth of oats in presence of xylose, nitrate, and phosphoric acid. It is probable that both bacteria reduce the nitrate to ammonia and also accumulate atmospheric nitrogen in the soil.

N. H. J. M.

Fermentation Experiments with Trehalose. By ARMINIUS BAU (*Chem. Centr.*, 1899, ii, 130—131; from *Woch. Brauerei*, 16, 305—306).—The constituent of certain yeasts which causes the break-

ing up of trehalose into dextrose must be of a nature differing from that of ordinary enzymes. Invertin has no effect on trehalose. It cannot be assumed that trehalose, which Bourquelot found in mould fungi, occurs in genuine yeasts. The hydration of trehalose is attributed to the living protoplasm or its constituents.

Trehalose is not suitable for distinguishing between different yeasts.

N. H. J. M.

Cellulose Enzymes. By FREDERICK C. NEWCOMBE (*Chem. Centr.*, 1899, ii, 129; from *Annals of Bot.*, 13, No. 49).—The extract of *Aspergillus Oryzae* attacks reserve cellulose more vigorously than starch; the enzymes of *Lupinus albus* and of *Phoenix dactylifera* behave similarly, but the latter hydrolyses somewhat more starch than *Lupinus albus*, whilst the enzyme acts very strongly on cellulose and less on starch than the extracts of *Lupinus* and *Phoenix*. The enzymes of barley malt, besides those already mentioned, attack cellulose when very much diluted. The effect of all these ferments is to render the cell-walls more and more transparent. The enzymes of *Lupinus* and *Phoenix* may be considered as cytase, and are not to be regarded as diastase.

N. H. J. M.

Raffinose as a Carbohydrate for the Nutrition of *Aspergillus Niger*. By HENRI GILLOT (*Chem. Centr.*, 1899, ii, 129—130; from *Bul. Acad. roy. Belg.*, 1899, 221—226).—When sucrose is employed for the nutrition of *Aspergillus niger*, it is inverted by a diastase before being assimilated, oxalic acid being formed as an intermediate product. In a similar manner, raffinose is inverted; the melibiose produced is further hydrolysed to dextrose and lævulose. Like sucrose, raffinose is completely utilised, and to the same extent in a given length of time. Oxalic acid is formed.

N. H. J. M.

Nitrogen Nutrition of Leguminous Plants. By JAN LUTOSLAWSKI (*Bied. Centr.*, 1897, 27, 688—689; from *Ber. physiol. Lab. landw. Inst. Univ. Halle*, 1898).—Peas were grown in pots containing sandy loam (6·6 kilograms) from a field on which peas had been grown the year before. Mineral manure was given to each pot, and to some sodium nitrate (1·277 grams) as well. Plants were taken up at five periods, (1) after the end of the germinating process (8th to 10th leaf), (2) commencement of flowering, (3) full flower, (4) after flowering, (5) ripe. The balance of nitrogen, taking into account the amounts in produce and in soil, gave the following gain per cent. of the original nitrogen in soil and seed (9·269 grams), (1) without, and (2) with nitrate at the different periods:

	I.	II.	III.	IV.	V.
1.	1·0	1·65	3·14	5·17	3·40
2.	0·0	1·45	1·89	2·95	2·20

In absence of nitrate, fixation of nitrogen commenced soon after the germinating period, whilst with nitrate it was later. For green manuring and for feeding, peas should be ploughed in or cut when fruit begins to be formed; or, in unfavourable weather, at earlier periods. Similar experiments with vetches failed in absence of nitrate.

N. H. J. M.

Chemistry of the Cell. By JAN SOSNOWSKI (*Chem. Centr.*, 1899, ii, 587; from *Centr. physiol.*, 13, 267—270).—The infusoriæ obtained from ordinary hay infusion are for the most part easily soluble in a 0.2 per cent. solution of an alkali hydroxide and in a 0.3 per cent. solution of sodium carbonate, only a few lustrous granules remaining undissolved. The solutions give the biuret reaction and the *Paramæcium* gives Millon's reaction. They are only attacked by pepsin-hydrochloric acid with difficulty. The extracts obtained by grinding the infusoriæ with quartz and treating with water, contain albumin which cannot be coagulated when the solutions are neutral, but is partly precipitated by adding sodium chloride or acids. The proteids are completely precipitated from the aqueous extract by barium hydroxide, and the precipitate contains phosphorus even after repeated treatment with dilute hydrochloric acid, alcohol, and ether. When the fat, lecithin, &c., have been removed from the cells by means of alcohol, only a portion of the residue is soluble in a 0.2 per cent. solution of sodium hydroxide, and the precipitate obtained by acidifying the alkaline solution with acetic acid contains phosphorus, gives the biuret reaction, and when boiled with phloroglucinol dissolved in hydrochloric acid exhibits the bands characteristic of the pentoses.

E. W. W.

Absorption of Iodine by Plants. By PAUL BOURCET (*Compt. rend.*, 1899, 129, 768—770).—Twenty-eight plants belonging to nine different natural orders were grown in carefully prepared soil containing 0.83 mg. of iodine per kilog., and when the plants reached maturity they were cropped, and the proportion of iodine in them was determined. It was found to vary from *nil* (potato, gherkin, black radish, parsley, carrots, chicory, endive) to 0.32 (green haricots), 0.38 (*Beta cyclo*), and even 0.94 (garlic) mg. per kilogram. Certain families, such as *Liliaceæ* and *Chenopodiaceæ*, absorb more iodine than others, such as *Solanaceæ* and *Umbelliferae*, but different species of the same order show considerable differences.

C. H. B.

Physiological Importance of Furfuroids in Sugar Beet. By JULIUS STOKLASA (*Chem. Centr.*, 1899, ii, 57—58; from *Zeit. Zucker-Ind. Böhmen*, 23, 387—397. Compare Abstr., 1899, ii, 792).—Inasmuch as pentosans are important constituents of the cell membranes, it may be concluded that they are formed from sucrose. As new organs containing pentosans develop in the second year of vegetation, the sucrose gradually disappears from the roots. In water-culture experiments with peas and maize, it was found that only a slight excess of furfuroids was produced in presence of sucrose as compared with dextrose; when, however, root heads of beet were fed under conditions of sterilisation with sucrose and dextrose respectively, in absence of carbon dioxide, it was found that a far greater amount of furfuroids was produced with sucrose than with dextrose. Potassium chloride assists the production of furfuroids.

Furfuroids are essential in the building up of cell membranes. The celluloses of the embryo are hydrolysed, and thus furnish the material for the production of the new hemicellulose group of the

seedlings. The hemicelluloses are transformed into lignocelluloses (which protect the roots from infection by parasitic fungi) and lignin substances.

N. H. J. M.

Occurrence of Indican in the Chlorophyll Grains of the Indigo Plants. By HANS MOLISCH (*Chem. Centr.*, 1899, ii, 482; from *Ber. deutsch. bot. Ges.*, 17, 228—233).—Indican is usually found in the mesophyll and external skin of the leaves of the indigo plant. Inside the green cell itself, it occurs mainly in the chlorophyll grains. It is best detected by converting it into indigo-blue by means of alcohol, ammonia, or chloroform vapour. The discovery of indican in the chlorophyll grains is the first proof of the presence of a glucoside containing nitrogen in the chlorophyll grains of the indigo plants.

E. W. W.

Histidine and Lysine in the Decomposition Products of the Proteid of Conifer Seeds. ERNST SCHULZE and ERNST WINTERSTEIN (*Zeit. physiol. Chem.*, 1899, 28, 459—464).—The proteid material of the seeds of various conifers has been shown to yield arginine on decomposition. The present research shows that, on decomposing the proteid with hydrochloric acid, histidine and lysine are also obtained. From 300 grams of dry material, 3 grams of histidine chloride, 19 grams of arginine nitrate, and 3 grams of lysine picrate were obtained.

W. D. H.

Histidine and Lysine in Seedlings. By ERNST SCHULZE (*Zeit. physiol. Chem.*, 1899, 28, 465—470).—From the present and previous work it is shown that from the seedlings of *Lupinus luteus* eight nitrogenous derivatives of proteid are obtainable, namely, asparagine, leucine, aminovaleric acid, tyrosine, phenylalanine, arginine, histidine, and lysine.

W. D. H.

Progressive Development of Essence of Bergamot. By EUGÈNE CHARABOT (*Compt. rend.*, 1899, 129, 728—731).—Analyses of two samples of essence of bergamot, one prepared from the green but fully developed fruit, and the other from the ripe fruit of the same trees, show that during the process of ripening, the free acids, calculated as acetic acid, decrease from 0.289 to 0.283, the total linalool from 40.5 to 35.5, the free linalool from 13.9 to 5.9, and the bergaptene from 5.9 to 5.5 per cent., whilst the linalyl acetate increases from 33.8 to 37.3 per cent. An increase is also observed in the terpenic constituents of the oil, but the relative proportions of limonene and dipentene remain unchanged. From these results, it is concluded that the primary development of the fruit is characterised by the active formation of linalool, and that during the subsequent ripening this reacts with the free acetic acid and is partly converted into linalyl acetate, partly dehydrated with the production of limonene and dipentene.

N. L.

Hazelnut Oil. By JOS. HANUŠ (*Chem. Centr.*, 1899, ii, 557—558; from *Zeit. Unters. Nahr.-Genussm.*, 2, 617—622).—From the ripe fruit of *Corylus avellana*, L., 50—60 per cent. of a clear, golden-yellow oil may be extracted by means of ether. It has a pleasant taste, an odour like

that of fresh butter, and the following constants: sp. gr., 0.9169 at 15°; saponification number, 193.7; iodine number, 90.2; Hehner's number, 95.6; Reichert-Meissl number, 0.99, and acetyl number, 3.2. The insoluble fatty acids have: saponification number, 200.6; iodine number, 90.6, and mean molecular weight of 279.0. The unsaturated fatty acids have: saponification number, 198.5; iodine number, 91.3; Maumene's number, 36.2, and mean molecular weight of 282. The oil does not give characteristic reactions with the usual reagents, but yields a greenish, semi-solid elaidin, and consists of 85 per cent. of oleic acid, 10 of palmitic and stearic acids, 10.41 of glycerol, and 0.5 of phytosterol. Oleic acid is the only unsaturated acid present, and the oil does not contain arachic acid. E. W. W.

Cortex Lokri. By W. P. H. VAN DEN DRIESSEN MAREEUW (*Chem. Centr.*, 1899, ii, 589; from *Ned. Tijd. Pharm.*, 11, 227—234).—The bark, *Cortex Lokri*, is obtained from *Hymenaea Courbaril*; it contains 2.7 per cent. of catechin, 23.6 of catechu-tannic acid, 0.6 of fat, and 7.6 of ash. E. W. W.

Saw Palmetto. By P. L. SHERMAN and C. H. BRIGGS (*Pharm. Archives*, 1899, 2, 101—116).—The saw palmetto (*Sabal serrulata*) is a tree which is found along the S.E. coast of the United States; the fruit is dark purple in colour, about the size of an olive, and consists of a juicy pulp and a very hard seed or nut. The fruit is pressed in a hydraulic press; when the juice is allowed to remain, an oil rises to the surface, in amount equal to about 1.5 per cent. of the fruit. This oil consists of acids, chiefly hexoic, octoic, decoic, lauric, palmitic, and oleic, and their ethyl esters, about 37 per cent. consisting of esters, the remainder of the free acids.

The dry nuts form 17.5 per cent. of the fruit; they were cracked, and the very hard kernels broken, ground to a meal, and extracted with boiling benzene; in this way, an oil was obtained in amount equal to about 2 per cent. of the fruit. This oil contained about 97.7 per cent. of glycerides of octoic, decoic, lauric, palmitic, stearic, and oleic acids, the rest consisting of the free acids.

The fruit contains in addition about 5.4 per cent. of sugar, estimated by its cupric reducing power, and calculated as invert sugar; also a small amount of pentoses. No alkaloid could be detected.

C. F. B.

Presence of an Oxidising Enzyme in the Vine. By CHARLES CORNU (*J. Pharm.*, 1899, [vi], 10, 342—343).—The vine contains an oxidising enzyme which belongs to the class of "aéroxydases," or enzymes, which only cause oxidation in the presence of air. The activity of the ferment is greater in the spring than in the autumn.

H. R. LE S.

Accumulation of Nitrogen by the Cultivation of Intermediate Crops on Loamy Soil. By MAX MAERCKER (*Bied.-Centr.*, 1899, 27, 655—656; from *Landw. Jahrb.*, 1898, 27, 157).—A mixture of beans (50), peas (100), and vetches (50 kilos. per hectare) accumulated 154.4 kilos. of nitrogen, whilst as much as 4624 kilos. of organic matter was produced on a hectare. The least favourable results

showed an accumulation of nitrogen corresponding with 5—6 cwt. of sodium nitrate. A mixture of lupins and lathyrus proved to be unsuitable for the soil.

In the dry season of 1898, the effect of the intermediate crop on the succeeding crop of oats was very striking, partly owing to the water supplied by the deep roots of the *Leguminosæ*.

N. H. J. M.

Experiments with Different Lupins. By A. SEMPOLOWSKI (*Bied. Centr.*, 1899, 27, 716; from *Fühling's Landw. Zeit.*, 1898, 47, 517).—The yield of corn (I) in kilos. per hectare, and (II) the percentage of alkaloids, was determined in the following varieties of lupins:—(1) *Lupinus angustifolius*, var. *fl. roseo*; (2) var. *fl. albo*; (3) *L. hirsutus*; (4) var. *fl. cæruleo*; (5) *L. angustifolius*; (6) *L. hirsutus*, var. *fl. albo*; (7) *L. albus*; (8) *L. luteus*, var. *semine nigro*; (9) var. *semine albo*; (10) *L. luteus*; (11) *L. perennis*.

	1.	2.	3.	4.	5.	6.	7.	8.	9.	10.	11.
I.	3321	3310	3236	3154	3088	2924	2708	1736	1717	1550	323
II.	0·430	0·345	0·378	0·378	0·641	0·378	0·250	0·290	0·788	0·833	—

The narrow leaved varieties gave the greatest yields; yellow lupins gave the least, and contained most alkaloids. *L. angust.* var. *fl.*, gave a high yield of corn, with a comparatively low percentage of alkaloids.

N. H. J. M.

[Experiments with] Cows at Lauchstädt, 1896—1897. By FRIEDRICH ALBERT (*Bied. Centr.*, 1899, 27, 663—667; from *Landw. Jahrb.*, 1898, 27, 188. Compare Abstr., 1899, ii, 689).—Experiments were made with 10 cows (two kinds) to ascertain the effect of food-fats on the production of milk and of milk fat. There were five experimental periods of 7—14 days, with longer intermediate periods for gradually changing the foods. The amounts of fat in the concentrated foods were as follows:—Period preceding the experiment (0·504 kilogram); (1) palm cake, 0·937 kilogram of fat; (2) lupins, 0·297; (3) cocoa nut cake, 0·747; (4) cocoa nut cake, (1·706); (5) lupins, 0·297 kilogram of fat.

Increasing the amount of fat in the food had no effect on milk production so long as the amount of fat did not exceed 1 per thousand of the live weight of the cows; with 1·706 kilograms of fat to 1000 kilograms of live weight the production of milk was considerably diminished.

Palm cake and cocoa nut cake increased the percentage of fat in the milk; with the largest amount of fat, the average increase was 0·75 per cent.; with rations (1) and (3) the percentage increase of fat in milk was 0·36 and 0·28.

The rations with low percentage of fat had very little effect on the percentage of fat in the milk, and the lupins affected the taste of the milk.

Feeding with large amounts of fat increased the live weight of the cows considerably; in the case of one breed, the cows became unwieldy and had to be killed. The rations with low percentage of fat caused great loss of weight,

N. H. J. M.

Experiments on Feeding Cows with Brewery Residues. By EBERH. RAMM and E. MÖLLER (*Bied. Centr.*, 1899, 27, 668—670; from *Milchzeit.*, 1899, 97).—The food contains brewery refuse and other materials, and consists of brown, worm-shaped lumps as hard as glass. It contains 42·48 per cent. of digestible proteids, 0·8 per cent. of fat, 26·96 per cent. of non-nitrogenous extract, and 1·3 per cent. of woody fibre.

Feeding experiments were made in which the cows received hay (14), straw (4·5), roots (50), and dried brewers' grains (4 kilograms for 1000 kilograms of live weight). In addition, they received either earth-nut cake (containing 6·5 per cent. of fat), or brewery residues (6 kilograms). After 14 days, the cows which had brewery residues weighed rather more than the others (average 1·97 kilograms), and had yielded 94 grams more milk but 33 grams less fat and 45 grams less dry matter in the milk per head per day. The percentage of fat in the milk was: with earth-nut cake 3·322, and with brewery residues 3·062. The butter, after feeding with (1) earth-nut cake and (2) brewery residues, contained: water, 27·7 and 16·0; fat, 70·91 and 82·10; casein, &c., 1·22 and 1·76; ash, 0·17 and 0·14 per cent. The examination of the fat showed the butter in both cases to be normal.

N. H. J. M.

Amounts of Plant Food withdrawn from Peaty and Sandy Soil by cutting Heather and Turf. By HEINRICH IMMENDORFF (*Bied. Centr.*, 1899, 27, 649—652; from *Landw. Jahrb.*, 1898, 27, iv, 503).—In order to ascertain the losses which moor-land undergoes where turf and heather are cut for litter, samples were taken from measured areas, both from peaty and sandy soil, the ordinary implements being employed. Determinations of the different constituents were then made. The results calculated to kilograms per hectare are as follows: (1) sandy soil, and (2) peaty soil:

Fresh substance.	Dry matter.	N.	K ₂ O.	CaO.	MgO.	Fe ₂ O ₃ , Al ₂ O ₃ .	P ₂ O ₅ .	SO ₃ .
32,500	20,858	179·7	53·4	72·7	31·0	64·6	22·4	40·4
48,750	21,231	201·5	34·0	89·2	40·3	78·6	19·1	53·1

The dry substance removed from the sandy soil consisted of vegetable matter (18,222) and humous sand (2636 kilograms).

Assuming the cutting to take place about every 15 years, it is seen that the land must be impoverished in a comparatively short time, and it is concluded that the benefits resulting from the practice by no means compensate for the injury done to the land.

N. H. J. M.

Amount of Humus in Soils, and the Percentage of Nitrogen in the Humus, as affected by the Application of Air-slaked Lime and other Substances. By HOMER J. WHEELER, C. L. SARGENT, and B. L. HARTWELL (*J. Amer. Chem. Soc.*, 1899, 21, 1032—1037).—Zinc vessels, with holes for drainage, were filled with soil, (254 lbs.), to which different manures were added. Maize was grown the first year, oats the second, and rye the third year. At the end of the experiment, humus, and nitrogen in the humus, were

determined. Nitrogen, as ammonia or nitrate, was applied to some pots at the rate of 2.65 grams per pot, lime at the rate of 4 tons per acre (147.2 grams per pot), and gypsum in amounts corresponding with the lime. All the manured pots had potassium chloride and dissolved bone black.

The percentage amounts of (1) humus nitrogen, and (2) humus in the dry soil, and (3) nitrogen in dry humus, were as follows :

No manure.	Am_2SO_4 .	Am_2SO_4 , CaO.	Am_2SO_4 , CaO.	Am_2SO_4 , CaO.	No N or CaO.	CaO.	NaNO_3 , CaO.	NaNO_3 , CaO.
1. 0.130	0.128	0.133	0.126	0.139	0.129	0.139	0.143	0.133
2. 3.86	3.93	3.77	3.63	3.65	3.75	3.51	3.93	3.42
3. 3.37	3.26	3.53	3.47	3.81	3.44	3.68	3.64	3.89

The results in the third column were obtained with 36.8 grams of CaO instead of 147.2 grams.

Potassium chloride and phosphoric acid alone (column 6) slightly decreased the humus and humus nitrogen. Lime and gypsum lowered the humus, but increased the nitrogen in the humus. Ammonium sulphate, without lime, reduced the nitrogen in the humus, whilst nitrate increased it.

It would seem that lime increased the amount of humus nitrogen, notwithstanding that the lime pots had yielded the heaviest crops. Although there was also a decrease in the amount of humus, there is probably no danger of injuring soil by the application of lime, as lime gives rise to greatly increased root production, when the land is laid down to grass for a few years.

It is thought probable that nitrates become converted into soluble organic compounds, probably by the intervention of denitrifying organisms. In presence of lime, as well as nitrate, the increase in humus nitrogen was less than with nitrate alone, owing, perhaps, to the destruction of denitrifying organisms by the lime.

N. H. J. M.

Losses of the Nitrogen of Stable Manure in Covered and Uncovered Stalls. By MAX MAERCKER and W. SCHNEIDEWIND (*Bied. Centr.*, 1899, 27, 656--657; from *Landw. Jahrb.*, 1898, 27, 215): **Conservation of Manure.** By W. SCHNEIDEWIND (*ibid.*, 658; from *Landw. Jahrb.*, 1898, 27, 234).—The loss of nitrogen in manure in stalls where animals are fattened was comparatively slight (13.2 per cent.) so long as they remain on it, but rose to 34.8 per cent. when the manure remained for 4 weeks without the animals. Manure should therefore be spread on the fields, or treated with a preservative, as soon as the animals leave the stalls.

The loss of nitrogen in uncovered and covered manure heaps was 37.4 and 36.9 per cent. respectively. The higher result, with covered heaps, is attributed to loss of moisture, greater concentration, and increased temperature. Heaps under cover should be kept moist and compact. Addition of slight excess of 0.5 per cent. sulphuric acid causes production of ammonia compounds from proteids.

In fattening experiments with sheep in stalls, the loss of manure nitrogen was again satisfactory, but the manure lost considerably after the sheep were removed.

As regards preservatives, it was found that marl (30 per cent.) reduced the loss of nitrogen from 22·6 to 9·9 per cent.; with marl (30) and peat litter (2 per cent.), the loss was 6·1 per cent. Sodium hydrogen sulphate (6 per cent.) reduced the loss of nitrogen to 1·3 per cent. and at the same time rather improved the quality of the manure by increasing the nitrogen directly available. N. H. J. M.

Bat Guano found at Cagliari, Sardinia. By GIULIO PARIS (*Chem. Centr.*, 1899, ii, 65; from *Staz. sper. agrar. ital.*, 32, 176—185. Compare Abstr., 1897, ii, 383).—The guano has the following percentage composition:—Moisture, 13·85; organic matter, 58·78; ammonia, 1·32; nitric acid, 0·75; uric acid, 0·63; Na_2O , 3·10; K_2O , 1·77; CaO , 1·72; MgO , 0·48; Fe_2O_3 and Al_2O_3 , 5·20; P_2O_5 (organic, citrate soluble, and insoluble respectively), 0·50, 4·20, and 0·66; SO_3 , 2·28; SiO_2 (soluble and insoluble in HCl , sp. gr. 1·11), 1·17 and 3·65; CO_2 , 1·80. N. H. J. M.

Value of Lime Compounds in Phosphatic Manures. By O. BÖTTCHER (*Bied. Centr.*, 1899, 27, 662—663; from *D. Landw. Presse*, 1899, 91, 222).—In reply to Ullmann (*ibid.*, No. 13), it is stated that the value of basic slag as a lime manure is not less at the present time than formerly; the amount of free lime is usually only slightly less.

Citric acid (2 per cent.) dissolved, in half an hour, 42—45 per cent. of lime; and in 12 hours, 45—52 per cent. N. H. J. M.

Analytical Chemistry.

Estimation of Oxygen in Water. By L. MUTSCHLER (*Chem. Centr.*, 1899, ii, 225; from *Zeit. Unters. Nahr.-Genussm.*, 2, 481).—The method consists in enclosing in a bottle of about a litre capacity three sealed glass tubes, one of which contains an alkali, the second a known volume of $N/10$ ferrous ammonium sulphate, and the third an excess of 50 per cent. sulphuric acid. The acid tube is attached to the caoutchouc stopper, the others lie at the bottom. After filling the bottle with the water, the two former are fractured by a glass ball and the ferrous hydroxide diffused through the water. After a sufficient time, the acid tube is also fractured and the unoxidised ferrous salt titrated with $N/10$ permanganate. M. J. S.

Estimation of Sulphur in Pig Iron. By M. J. MOORE (*J. Amer. Chem. Soc.*, 1899, 21, 972—975).—In the estimation of sulphur in pig iron, much less sulphur is always obtained by the volumetric process than by the gravimetric method.

The practice of pouring the molten metal into water and obtaining a "shot sample" is not a good one; it is preferable to catch a small test in a sand mould. L. DE K.

Estimation of Sulphur in Petroleum. By SIEGFRIED FRIEDLÄNDER (*Chem. Centr.*, 1899, ii, 406—407; from *Arbb. Kais. Ges.-A.*, 15, 365—372).—The sample is burnt in an Ohlmüller lamp, which is weighed before and after the experiment, the products of combustion being drawn through two wash-bottles containing a 5 per cent. solution of potassium hydrogen carbonate. The solution is then oxidised by means of potassium permanganate and hydrochloric acid, and the sulphuric acid estimated as usual.

L. DE K.

Estimation of Sulphur in Petroleum. By SIEGFRIED FRIEDLÄNDER (*Chem. Centr.*, 1899, ii, 629—630; from *Chem. Ind.*, 22, 343—349).—Equally good results are obtained by the use of the apparatus and processes of Heusler, Engler, Kiessling, or Ohlmüller, but the latter is by far the quickest, it being possible to effect an analysis in half an hour. Attention is called to the occasional presence of sulphur compounds in the air, and to the means for removing them.

L. DE K.

Estimation of Sulphur in Naphtha. By ALEXANDER P. LIDOFF (*Chem. Centr.*, 1899, ii, 493; from *J. Russ. Chem. Soc.*, 1899, 31, 567—570).—1 gram of the sample is dissolved in ether and carefully mixed with 30 grams of a mixture of 17 parts of potassium nitrate and 13 parts of sodium carbonate. When the ether has completely evaporated, the mixture is put by small degrees into a platinum dish heated to redness. The fused mass contains the sulphur as sulphate, which is then estimated in the usual way.

L. DE K.

Estimation of Sulphur in Organic Substances. By ROBERT HENRIQUES (*Chem. Zeit.*, 1899, 23, 869).—The process recommended for the estimation of total sulphur in rubber wares may be safely used for the analysis of other not readily volatile organic substances (compare this vol., ii, 123).

L. DE K.

Detection of Nitrogen in Organic Compounds containing Sulphur. By ERNST TÄUBER (*Ber.*, 1899, 32, 3150—3154).—Jacobsen's method (*Ber.*, 12, 2318) which consists in adding iron-powder to the substance before heating with potassium, is entirely untrustworthy, since the addition of the iron greatly facilitates the absorption of nitrogen from the air, and cyanides are formed even when the substance contains no nitrogen; the method is useless unless carried out in a stream of hydrogen. Magnesium has a similar, but very slight, effect in facilitating the absorption of nitrogen; tungsten, chromium, and nickel are still less effective, and copper produces no effect at all. The method recommended consists in using a large excess of potassium and then an excess of ferric chloride to oxidise the potassium sulphide which is formed.

T. M. L.

NOTE.—The inaccuracy of Jacobsen's method was pointed out at the time by Remsen (*Abstr.*, 1880, 473).—EDITORS.

New Method for Estimating Nitric Acid. By J. F. POOL (*Chem. Centr.*, 1899, ii, 227; from *Nederl. Tijdschr. Pharm.*, 11, 171).—The nitrate is evaporated to dryness with excess of sodium chloride

in a flask. The air is expelled by carbon dioxide, and concentrated sulphuric acid is introduced; water is added and the gases are driven over by boiling into a solution of potassium iodide. The liberated iodine is then titrated. M. J. S.

Estimation of Phosphorus by Reed's Method. By D. GERHARDT (*Chem. Centr.*, 1899, ii, 227; from *Nederl. Tijdschr. Pharm.*, 11, 174).—Reed's method (Abstr., 1899, ii, 451) depends on the fact that phosphorus dissolved in carbon disulphide combines with 5 atoms of bromine in presence of alcohol. The author finds that the presence of alcohol is not necessary; in a simple carbon disulphide solution 5 atoms of bromine are absorbed, not 3, as stated by Reed. The method is useless in presence of fats. M. J. S.

Estimation of Phosphorus in Organic Compounds. By CH. MARIE (*Compt. rend.*, 1899, 129, 766—767).—The substance is oxidised by nitric acid and potassium permanganate, the phosphoric acid precipitated with ammonium molybdate, the precipitate washed until quite free from manganese, redissolved in ammonia, and precipitated with magnesia mixture. The ammonium magnesium phosphate should be washed until the filtrate gives no coloration when treated with excess of hydrochloric acid, a small quantity of ammonium thiocyanate, and a fragment of zinc.

15 to 20 c.c. of concentrated nitric acid are used for each gram of substance, heated on a water-bath, and from 5 to 6 grams of finely powdered potassium permanganate are added in successive small portions until the liquid remains red for several minutes. Excess of permanganate is decomposed by adding a small quantity of sodium or potassium nitrite. Even compounds difficult to oxidise by Carius' method are readily dealt with in this way. C. H. B.

Separation of Barium, Strontium, and Calcium by Mixed Carbonate and Sulphate Solutions of varying Composition. By FRIEDRICH W. KÜSTER (*Zeit. anorg. Chem.*, 1899, 22, 161).—A short criticism of Morgan's theoretical calculations (Abstr., 1899, ii, 627). The author points out that in the calculation of the solubility product, Morgan has entirely neglected the effect of the hydrolysis on the barium carbonate solution. E. C. R.

Composition of Ammonium Magnesium Phosphate. By HUGO NEUBAUER (*Zeit. anorg. Chem.*, 1899, 22, 162), and by FRANK A. GOOCH and MARTHA AUSTIN (*ibid.*, 163).—Neubauer claims priority in determining the composition of the magnesium ammonium phosphate precipitated in the usual method of estimation, and Gooch and Austin admit the justness of his claim (compare Neubauer, Abstr., 1893, ii, 236, 489; 1896, ii, 73, 674). E. C. R.

Analysis of "Weissmetall." By H. NISSENSON (*Chem. Zeit.*, 1899, 23, 868—869).—This alloy consists chiefly of lead with tin and antimony. It is dissolved in dilute nitric acid containing tartaric acid, sulphuric acid added, and the nitric acid expelled by heat, taking care not to char the tartaric acid. It is then diluted with water and the undissolved lead sulphate collected, the filtrate rendered alkaline

with aqueous caustic soda, excess of sodium sulphide added, and the whole boiled and filtered from any copper sulphide. The liquid is then electrolysed at 80° , using a current of 3 volts and 1.5 ampères, when the antimony is deposited. To obtain the tin, sufficient ammonium sulphate is added to convert all the sodium sulphide into the ammonium compound and the liquid again electrolysed. L. DE K.

Electrolysis of Metallic Phosphate Solutions. By HARRY M. FERNBERGER and EDGAR F. SMITH (*J. Amer. Chem. Soc.*, 1899, 21, 1001—1007).—The best conditions for the separation of copper from iron, aluminium, chromium, cobalt, zinc, nickel, or manganese in phosphoric acid solution have been determined.

In every case, a solution containing a little over 0.1 gram of each metal was employed, the phosphate was precipitated by adding 30—60 c.c. of disodium hydrogen phosphate solution of sp. gr. 1.0358, then dissolved by adding 5—10 c.c. of phosphoric acid solution of sp. gr. 1.347, and the solution electrolysed with a normal current density of from 0.035—0.072 ampère and a voltage of 1.5—2.6. In each case, the amount of liquid was 225 c.c., the time occupied 5 to 7 hours, and the temperature was kept at 60 — 70° .

Nickel may also be deposited from phosphoric acid solution by employing a current of 0.5 ampère and 7—8 volts. It has been found impossible to completely separate nickel from manganese, chromium, or zinc, mercury from cadmium or uranium, and copper from uranium. Mercury may, however, be separated from zinc. J. J. S.

Analysis of Bronzes. By A. FOMIN (*Chem. Centr.*, 1899, ii, 495—496; from *J. Russ. Chem. Soc.*, 31, 565—567).—About 0.3 gram of bronze filings, freed from iron particles by aid of a magnet, is treated with nitric acid. Ammonium nitrate is added and the whole evaporated to dryness. The residue is treated with water, neutralised with ammonia, and again acidified with nitric acid, and the insoluble matter, consisting of tin oxide slightly contaminated with antimony, iron, and traces of copper, is removed by filtration.

The filtrate, measuring about 100 c.c., is mixed with 30 drops of nitric acid and submitted to electrolysis by means of a current of 0.14—0.34 ampère and 2 volts. After 3—4 hours, 5 c.c. of saturated solution of ammonium nitrate are added, and in 24 hours the operation is finished. The electrodes are washed twice with water and once with alcohol. The one with the copper deposit is dried quickly, and the other, coated with lead dioxide, is dried for 15 minutes at 180° . Iron is then searched for in the usual way. L. DE K.

Estimation of Manganic Acids in the presence of Manganese Salts or of both Manganese Compounds in the presence of each other, by means of an Alkaline Solution of Arsenious Acid. By C. REICHARD (*Chem. Zeit.*, 1899, 23, 867—868).—Aqueous sodium hydroxide is added in sufficient quantity to precipitate the manganese salts as manganous or manganomanganic hydroxide. Standardised alkaline solution of arsenious acid is then added and the operation is conducted as previously described (*Abstr.*, 1899, ii, 813).

The residue left on the filter is then ignited and weighed; the difference in the total manganese and that found by titration represents the manganese salts.

Two other processes are also suggested, but not supported by experiments.

L. DE K.

Estimation of Chromium in Iron and Steel. By E. DÖHLER (*Chem. Zeit.*, 1899, 23, 868).—The sample is dissolved in hydrochloric acid, and from this solution the chromium is precipitated by repeated treatment with excess of barium carbonate in a closed flask. The precipitate is then fused in a porcelain crucible with potassium nitrate and potassium sodium carbonate, and the chromium estimated in the aqueous extract in the usual manner.

L. DE K.

Estimation of Chromium in Steel. By R. W. MAHON (*J. Amer. Chem. Soc.*, 1899, 21, 1057—1060).—This is a slight modification of McKenna's process based on the oxidation of chromium to chromic acid by means of nitric acid and potassium chlorate, and titration with ferrous sulphate and potassium permanganate.

Nitric acid and potassium chlorate are employed in greatly reduced quantities, and paper instead of asbestos is used as a filtering medium.

L. DE K.

Detection of Alkali Chromates in Milk. By ALEXANDRE LEYS (*J. Pharm.*, 1899, [vi], 10, 337—340).—The white ash obtained by the evaporation and subsequent ignition of 100—150 c.c. of the milk is moistened with distilled water and filtered. A portion of this filtrate is added to 5 c.c. of pure concentrated hydrochloric acid, previously coloured with indigo-carmin, when, if a chromate is present, the solution will be immediately decolorised. A second portion of the filtrate is added to 5 c.c. of an acetic acid solution of pure aniline and commercial toluidine, when, if a chromate is present, a cherry-red coloration, due to magenta, will be produced on heating. These reactions only prove the presence of an oxidising substance, and in order to further identify the chromate, the rest of the filtrate is acidified with dilute sulphuric acid and a few drops of a solution of hydrogen peroxide added, when the production of a blue coloration fully proves the presence of a chromate.

H. R. LE S.

Iodometric Estimation of Gold. By FRANK A. GOOCH and FREDERICK H. MORLEY (*Amer. J. Sci.*, 1899, 8, 261—266).—Contrary to Peterson's statement that gold chloride cannot be estimated by the iodine set free when it is treated with potassium iodide, the authors have found this to be a very accurate method for the estimation of very small quantities of gold.

The gold, which should be in the metallic state and not exceed 0.01 gram, is dissolved in chlorine water, and the excess of chlorine is then removed by adding ammonia, boiling and acidifying with hydrochloric acid; this treatment should be repeated. After diluting to 200 c.c., 10 c.c. of the liquid are mixed with 0.02 gram of potassium iodide, and the liberated iodine then found by titrating with *N*/1000 solution of sodium thiosulphate, using starch as indicator; it is advisable

to add a very slight excess and then to titrate back with $N/1000$ solution of iodine.

L. DE K.

Parting of Gold Platinum Alloy. By EDUARD PŘIWOZNIK (*Chem. Centr.*, 1899, ii, 539; from *Oesterr. Zeit. Berg.-Hütt.*, 47, 356—358).—The following process is used in the imperial Austrian assay office. The alloy is first treated with nitric acid of sp. gr. 1.199, which also dissolves a little of the platinum if silver is present. The mass is then treated with diluted *aqua regia* (100 c.c. of strong hydrochloric acid, 43 c.c. of strong nitric acid, and 143 c.c. of water), which dissolves the gold with moderate ease, but does not perceptibly attack the platinum. If there should be any silver left, the metal gets coated with silver chloride and the gold is prevented from dissolving; in that case, the liquid is poured off and the silver chloride removed by means of ammonia. The gold solution is heated with hydrochloric acid until the nitric acid is expelled, and the platinum then precipitated with excess of ammonium chloride.

If the alloy is composed of gold, silver, and platinum, each in large proportion, it must be fused with thrice its weight of zinc; after treating with sulphuric acid, the undissolved mass is treated as just directed.

L. DE K.

Method and Apparatus for Incinerating Vegetable and Animal Substances. By A. E. SHUTTLEWORTH and BERNHARD TOLLENS (*Chem. Centr.*, 1899, ii, 144; from *Jahrb. Landw.*, 47, 173).—Addition of calcium acetate prevents the sintering which so often forms an obstacle to complete incineration. The authors have devised a special platinum apparatus (not described) by the use of which the time necessary for incineration is much shortened, and volatilisation of chlorides is prevented.

M. J. S.

Tucker (this vol., ii, 52) has described a modified form of this apparatus.—EDITORS.

Application of the Kjeldahl Method of Destroying Organic Substances in the Detection of Metals. By OTTO GRAS and WILHELM GINTL, jun. (*Chem. Centr.*, 1899, ii, 145; from *Oesterr. Chem. Zeit.*, 2, 308).—Halenke's process (*Abstr.*, 1899, ii, 696) is especially suitable for the examination of coal-tar dyes. 10 grams of the substance is heated for 6—8 hours with 60—80 c.c. of sulphuric acid containing 10 per cent. of potassium sulphate, with final addition of some potassium nitrate. After diluting and warming, the solution is ready to be examined for metals.

M. J. S.

Estimation of Ferrocyanides in Spent Gas-purifying Material. By RUDOLF RIECHELMANN (*Chem. Centr.*, 1899, ii, 144; from *Zeit. öffentl. Chem.*, 5, 188).—The methods of Donath and Margosches (*Abstr.*, 1899, ii, 527) and that of Knublauch (*Abstr.*, 1890, 87) do not yield concordant results, since the former expresses as ferrocyanogen the iron soluble in other forms in the alkaline solution.

M. J. S.

Improvement in Trillat's Process for the Detection of Methyl Alcohol in Alcohols. By JULES WOLFF (*Chem. Centr.*, 1899, ii, 229—230; from *Ann. chim. anal. appl.*, 4, 183).—Pure ethyl

alcohol when treated by Trillat's process (Abstr., 1899, ii, 130) yields a condensation product which gives an identical reaction with that from methyl alcohol, but the former is not produced at atmospheric temperatures or below 60°. The following modification is therefore proposed: 100 c.c. of the alcohol is distilled; the first 10 c.c. are mixed with a solution of 15 grams of potassium dichromate in 130 c.c. of water and 70 c.c. of sulphuric acid (1:5); after 20 minutes, the mixture is distilled, the first 25 c.c. are rejected, and 50 c.c. from the following 100 c.c. are mixed with 1 c.c. of dimethylaniline and left at the ordinary temperature for 24 hours. After adding a little phenolphthalein, the liquid is accurately neutralised with soda and 30 c.c. distilled from it. To the residue there are added 25 c.c. of water and 1 c.c. of acetic acid, and the colour produced by lead peroxide is observed.

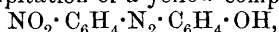
M. J. S.

Estimation of Alcohol in the Blood and Tissues. By NESTOR GRÉHANT (*Compt. rend.*, 1899, 129, 746—748).—See this vol., ii, 95.

Bromination of Phenols.—By WILHELM VAUBEL (*Zeit. angew. Chem.*, 1899, 1031—1032. Compare Abstr., 1893, i, 560; 1894, i, 19, 453; 1895, i, 55; 1896, i, 147, ii, 507).—A reply to Ditz and Cedivoda (this vol., ii, 54).—The author claims that good results are obtained by his method when a large excess of acid is present during the bromination and titration.

J. J. S.

Estimation of Carbohc Acid and other Phenols. By E. RIEGLER (*Chem. Centr.*, 1899, ii, 322; from *Bull. soc. sci. Bucuresci*, 8, 51—53).—50 c.c. of the aqueous solution, containing not more than 0.1 gram of the phenol, are mixed with 10 c.c. of a 5 per cent. solution of sodium hydroxide and 20 c.c. of diazo-solution. The red solution is now gradually acidified with dilute sulphuric acid (1:5), which causes the precipitation of a yellow compound,



which is washed, dried at 100°, and weighed; it is practically insoluble in water, 100 c.c. only dissolving 0.0002 gram.

The diazo-solution is prepared by mixing 5 grams of *p*-nitraniline, 25 c.c. of water, and 6 c.c. of sulphuric acid; 100 c.c. of water and 3 grams of sodium nitrite dissolved in 25 c.c. of water are then added, and the whole diluted to 200 c.c. The reagent must be kept in a dark place.

L. DE K.

New Method for the Gravimetric Estimation of Sugars. By PH. CHAPPELLE (*J. Pharm.*, 1899, [vi], 10, 395—398).—The sugar solution and 25 c.c. of Fehling's solution are placed in the tube of a centrifugal machine, diluted to 37.5 c.c., and heated in a calcium chloride bath at 110° for 6 minutes, in the case of dextrose solutions, and 10 minutes for lactose solutions. The whole is then whirled in the centrifuge for 3—4 minutes, and the liquid poured off from the precipitate, which adheres firmly to the sides of the tube. Boiling water is then added, and the whole again whirled. The water is then poured off, the tube and precipitate rapidly dried at 150—180° for 5 minutes and weighed. The method is rapid, and is applicable to the estimation of sugar in milk, urine, or gastric juice, from which

the proteids have been previously removed. The method is also applicable to the estimation of sugar by means of Sachsse's solution.

H. R. LE S.

Influence of Lead Acetate and Basic Acetate on the Estimation of Reducing Sugars in Wines and Lees. By HENRI PELLET (*Chem. Centr.*, 1899, ii, 573—574; from *Ann. chim. anal. appl.*, 4, 256—257).—Normal lead acetate is recommended in place of the basic salt in clarifying wines for polarisation, as the latter precipitates some of the sugar and so causes low results.

L. DE K.

Estimation of Sugar in Urine. By HENRI PELLET (*Chem. Centr.*, 1899, ii, 574; from *Ann. chim. anal. appl.*, 4, 256—257).—When preparing urine for polariscopic purposes, it is best to clarify with normal lead acetate or mercuric nitrate.

When using basic lead acetate, there is a danger that loss of sugar may occur, especially if the urine is neutral or alkaline.

L. DE K.

Estimation of Invert Sugar in the Presence of Sucrose. By H. JESSEN-HANSEN (*Chem. Centr.*, 1899, ii, 574; from *Compt. rend. trav. Lab. Carlsberg*, 1899, 103).—By operating as follows, the reduction of the alkaline copper solution by sucrose is reduced to a minimum: 10.4 grams of potassium sodium tartrate are dissolved in 15 c.c. of Kjeldahl's aqueous caustic soda, 15 c.c. of copper solution are added, and then the saccharine liquid; the whole is heated for 5 minutes on the boiling water-bath, a current of hydrogen being transmitted meanwhile.

L. DE K.

Estimation of Starch in Yeast. By GUSTAVE BRUYLANTS and H. DRUYTS (*Chem. Centr.*, 1899, ii, 154—155; from *Bull. assoc. Bely. Chim.*, 1899, 20).—The yeast is diffused in water, and the starch iodised by addition of a solution of iodine in potassium iodide. Its specific gravity is thereby increased and its tendency to ferment diminished. Any cell-residues are removed by passing the liquid through a silk sieve, and the mixture is allowed to deposit in a cylindrical glass vessel. As soon as the blue sediment becomes covered with a thin layer of yeast, the upper liquor is decanted and water added. The washing is continued until the microscope shows only traces of yeast. Hydrochloric acid is then added until the liquid contains 2 per cent. of acid, the mixture is heated until the starch dissolves and a small quantity of potassium sulphite added.

M. J. S.

Estimation of Glycogen. By ARMAND GAUTIER (*Compt. rend.*, 1899, 129, 701—705. Compare this vol., i, 81).

Detection of Acetic Acid in Urine. By V. ARNOLD (*Chem. Centr.*, 1899, ii, 146—147; from *Wien. Klin. Woch.*, 12, 541).—1 gram of *p*-aminoacetophenone is dissolved in 80—100 c.c. of water with addition of hydrochloric acid; a 1 per cent. solution of sodium nitrite is also required. 2 vols. of the former solution and 1 vol. of the latter are mixed, and 3 vols. of urine are added with 2—3 drops of strong ammonia. All urines give a more or less intense brownish-red coloration, which, on addition of 10—12 vols. of concentrated hydro-

chloric acid, passes into purple violet if acetic acid is present, but otherwise into yellow. Dark coloured urines are first decolorised by animal charcoal.

For the detection of bilirubin, an excess of aniline-*p*-sulphonic acid is added to 1 per cent. hydrochloric acid; then to 4 c.c. of this liquid, mixed with 0.5—1 c.c. of a 5 per cent. sodium nitrite solution and 50 c.c. of water, there is added $\frac{1}{3}$ —1 vol. of the urine. In presence of bile colouring matters, the mixture becomes orange-red, and on addition of a few drops of strong hydrochloric acid, violet. *p*-Diazobenzenesulphonic acid, which, as well as *p*-aminoacetophenone, can be employed for the detection of ethyl acetate in ether, does not give so marked a reaction with free acetic acid. M. J. S.

Estimation of the Insoluble Fatty Acids in Butter, and the Cause of Differences in the Results. By V. MAINSBRECK (*Chem. Centr.*, 1899, ii, 154; from *Rev. intern. falsific.*, 12, 87).—The want of agreement in the results obtained by different analysts in the estimation of the Hehner value appears to be due to differences in the time of heating and the amount of washing. From the author's experiments the loss amounts to 0.7 per cent. for each one and a half hours boiling. Litmus paper is not sufficiently sensitive for ascertaining the point of complete washing. In one experiment, 0.6 per cent. was removed by washing, and titration of the washings with *N*/10 alkali and phenolphthalein proved the continuous removal of soluble acids, after litmus ceased to show any acid reaction. It is therefore recommended that there should be a general agreement respecting the time of heating, and that the washing should be continued until 100 c.c. (with phenolphthalein) requires only 0.2 c.c. of *N*/10 alkali. M. J. S.

Estimation of Succinic Acid in Fermented Liquids. By J. LABORDE and L. MOREAU (*Ann. de l'Inst. Pasteur*, 1899, 13, 657—664).—When a solution containing succinic acid and glycerol is evaporated on the water-bath, a part of the succinic acid is converted into its glyceryl ester. This accounts for the low results obtained in the estimation of succinic acid in wines or other fermented liquids which invariably contain glycerol. This difficulty may be overcome thus: the succinic acid separated from the liquid is first titrated with decinormal alkali, and then the esters are hydrolysed by a known volume of decinormal alkali, and when the hydrolysis is complete the excess of alkali is titrated with decinormal acid. Only a small part of the succinic acid present in fermented liquids exists in the free state, the greater portion being present as a salt, from which the whole of the acid may be liberated by the addition of tartaric acid or potassium hydrogen sulphate. Tartaric acid is, however, slightly soluble in ether, and the amount dissolved by the ether must consequently be determined. This is done by converting the neutral tartrate into the acid tartrate by adding acetic acid and alcohol to the liquid which has been titrated, evaporating to dryness, and estimating the acid tartrate thus formed by titrating with decinormal alkali.

If the fermented liquid, in which succinic acid is to be estimated, contains more than 1 per cent. of sugar, it is evaporated to a syrup, 10 to 20 c.c. of alcohol are added, and the succinic acid separated by repeated extraction with ether. H. R. LE S.

Colour Reaction for Tartaric Acid and its Compounds. By JULES WOLFF (*Chem. Centr.*, 1899, ii, 569; from *Ann. chim. anal. appl.*, 4, 263).—Attention is called to a forgotten test for tartaric acid. A few centigrams of resorcinol are heated in a porcelain capsule with a little sulphuric acid until fumes are given off and the tartrate is added, when an intense dark red coloration is obtained. Neither oxalic nor citric acid gives the reaction. L. DE K.

Detection of Urochloralic Acid in Urine after Administration of Chloral Hydrate, especially in Cases of Poisoning. By DIOSCORIDE VITALI (*Chem. Centr.*, 1899, ii, 147; from *Boll. Chim. Farm.*, 1899, 38, 377).—The urine is concentrated to half its volume, and treated with a small excess of lead acetate and ammonia to feeble alkaline reaction. The precipitate of lead urochloralate is washed, then warmed with dilute sulphuric acid, and the filtrate cohobated for half an hour with zinc powder and sulphuric acid. The trichloroethyl alcohol resulting from the hydrolysis of urochloralic acid is thereby reduced to ethyl alcohol, which, after removal of the zinc by sodium carbonate, can be distilled over lime and recognised by odour, inflammability, conversion into iodoform, and into acetaldehyde (which may further be confirmed by Rimini's reaction), and by Vitali's reaction (treatment with carbon disulphide, potash, ammonium molybdate, and excess of dilute sulphuric acid, which produce the red colour of molybdenum xanthate). M. J. S.

Modified Soxhlet Apparatus for the Extraction of Fats from Liquids. By ALONZO ENGLEBERT TAYLOR (*Amer. J. Physiol.*, 1899, 3, 183—185).—The apparatus, which is figured and fully described, is stated to extract fat from solutions much more effectively than the Soxhlet apparatus, or the modifications of that instrument which have been hitherto devised. W. D. H.

Butter and Butter Substitutes. By W. G. INDEMANS (*Chem. Centr.*, 1899, ii, 495; from *Ned. Tijds. Pharm.*, 11, 219—226).—The chief points in butter analysis are, *A*, The number of molecules in a definite quantity of fat. *B*, The amount of olein. *C*, The solubility of the fatty acids in water.

The density, the electric resistance, the saponification number, the refractometer number, and the critical temperature of solution depend on *A*; the Hübl and Asboth's numbers depend on *B*; the melting and solidifying points depend on *A* and *B*, and the Reichert-Meissl and the Hehner-Angell numbers depend on *C*. As regards the number of molecules and the small amount of olein, butter-fat is surpassed by Ceylon oil, as it is also in density, electric resistance, and refractometer indication. The chief point of difference of butter from its surrogates, however, consists in the high percentage of fatty acids soluble in water and of the volatile acids; the latter vary with the season. L. DE K.

Rancidity in Butter-fat. By C. A. BROWNE, jun. (*J. Amer. Chem. Soc.*, 1899, 21, 975—994).—The so-called rancidity of fats is a much more complex phenomenon than hitherto believed.

As the rancidity of butter-fat increases, a decided increase in the acid, saponification, and Reichert numbers takes place; also a slight

increase in the ether number and a very marked decrease in the iodine absorption. Finally, an increase is noticed in the acetyl number and a decrease in the percentage of soluble acids and glycerol.

The physical constants of butter-fat, such as the specific gravity, refractive index, and heat of combustion, are also affected by rancidity.
L. DE K.

The Becchi Test. By ALPH. VAN ENGELEN (*Chem. Centr.*, 1899, ii, 147—148; from *Rev. intern. falsific.*, 12, 90).—Several variations in the mode of applying this test are in use. The author shows that in applying it to the free fatty acids (Millieau's method) the presence of small quantities of free mineral acid is prejudicial; the fatty acids must therefore be thoroughly washed with hot water, and the form of the test in which the reagent is acidified with nitric acid should be abandoned. To ascertain whether cotton-seed oil could be detected in the butter of cows fed with cotton-seed cake, two reagents were employed. The first consisted of 1 gram of silver nitrate dissolved in the smallest quantity of water and mixed with 200 c.c. of absolute alcohol; the second, of a solution of 1 gram of silver nitrate, 250 c.c. of 98 per cent. alcohol, 40 c.c. of ether, and 0.2 c.c. of nitric acid. The fat was dissolved in an equal volume of amyl alcohol, mixed with 1 c.c. of the reagent, and heated in the water-bath for 15 minutes. With the first reagent, the butter gave a coffee-brown, with the second a lemon-yellow, coloration. These reactions, and others obtained with the fatty acids, are not regarded as decisive of the question.

M. J. S.

Becchi's Test for Cotton-seed Oil. By PAUL SOLTSIEN (*Chem. Centr.*, 1899, ii, 539; from *Zeit. öffentl. Chem.*, 5, 306—308).—The Becchi silver reduction reaction is chiefly due to the presence of sulphur, this occurring in decided amount in samples of cotton oil which have been extracted from the seed by means of light petroleum; oil obtained by pressure contains but a trace of sulphur, and it loses this on heating at 200°.

In the original Becchi test, it was recommended that some rape oil should be added to intensify the reaction; this must, however, previously be heated at 150° to desulphurise it.
L. DE K.

Baudouin's Reaction. By WILHELM KERP (*Chem. Centr.*, 1899, ii, 228—229; from *Zeit. Unters. Nahr.-Genussm.*, 2, 473).—Commercial furfuraldehyde requires to be purified by two distillations under reduced pressure; a dilute alcoholic solution keeps well in completely filled bottles in the dark. The production of a violet coloration with hydrochloric acid alone depends both on the strength of the furfuraldehyde solution and on the amount of acid added. When the solution is sufficiently dilute and the quantity of acid small enough, the violet colour is not produced immediately, whilst the sesamé oil reaction is both more rapid and more sensitive. The concentration of the acid is also of importance. Acid of sp. gr. 1.127 gives the Baudouin reaction, but produces no violet colour in the absence of sesamé oil; a stronger acid (1.16) may be used in doubtful cases. Heating must be avoided. The lower limit of the reaction is at a dilution of 0.2 per cent. of

sesame oil : it follows that 2—2.5 grams of the oil can be detected in a kilogram of butter. The method cannot, however, be used as a quantitative colorimetric one. The behaviour of the red substance with various solvents is described, and some notes on its absorption spectrum are given. M. J. S.

Colour Tests for Sesamé Oil : Three New Characteristic Tests. By J. BELLIER (*Chem. Centr.*, 1899, ii, 453—454; from *Ann. chim. anal. appl.*, 4, 217—220).—The known tests are criticised. Behrens' reagent, a mixture of equal parts of sulphuric and nitric acids, is said to give better results if made of 100 c.c. of sulphuric acid, 10 c.c. of nitric acid, and 50 c.c. of water.

As new tests are proposed: *Ammonium vanadate*.—100 c.c. of sulphuric acid, 50 c.c. of water, and 2 grams of ammonium vanadate; this, on shaking with sesamé oil, gives a green colour, gradually becoming blackish. *Formaldehyde*.—100 c.c. of sulphuric acid, 50 c.c. of water, and 10 c.c. of 40 per cent. formaldehyde. Equal volumes of this reagent and sesamé oil gives, on shaking, a permanent bluish-black colour; an admixture of 1 per cent. of sesamé oil in olive oil may thus be detected. *Resorcinol*. 2 c.c. of the suspected oil is put into a test-tube, 2 c.c. of a saturated solution of resorcinol in benzene are added, and then 2 c.c. of nitric acid of sp. gr. 1.38 free from nitrogen oxides. In the presence of sesamé oil, an intense violet-blue or greenish-blue coloration is obtained. L. DE K.

Estimation of Formaldehyde in the Air. By M. WINTGEN (*Chem. Centr.*, 1899, ii, 454—455; from *Hygien. Rdsch.*, 9, 753—757).—A controversy with Peerenboom on the subject of the estimation of formaldehyde in the air by Romijn's process (*Abstr.*, 1898, ii, 166). With care, this process gives satisfactory results. L. DE K.

Detection of Aldehydes in Alcohols. By CONSTANTIN I. ISTRATI (*Chem. Centr.*, 1899, ii, 148—149; from *Rev. intern. falsific.*, 12, 91).—Barbe and Janvier's method (*Ann. chim. anal. appl.*, 1, 325), as improved by the author, consists in mixing exactly 2 c.c. of the alcohol with 0.2 c.c. of a saturated alcoholic solution of the special reagent, and pouring 1 c.c. of sulphuric acid down the side of the test-tube. The colours produced are observed immediately, then half an hour later with gentle shaking, then after thorough mixing, and, finally, after addition of 10 c.c. of water. The colours produced by such reagents as pyrogallol, α - and β -naphthols, phenylhydrazine, quinol, guaiacol, &c., with various aldehydes are given. M. J. S.

Estimation of Carvone in Volatile Oils. III. By F. W. ALDEN and S. NOLTE (*Pharm. Archives*, 1899, 2, 81—91).—In a 500 c.c. flask, fitted with a reflux condenser, 10 grams of the oil, 25 c.c. of alcohol, 5 grams of hydroxylamine hydrochloride, and 6.5 grams of sodium hydrogen carbonate are boiled together for $\frac{1}{4}$ — $\frac{1}{2}$ hour on the water-bath, only a small surface of the flask being heated; 25 c.c. of water are then added, the alcohol and much of the limonene distilled off on the water-bath, and then steam is passed through, the distillate being collected in fractions of 5—10 c.c. in test-tubes until it is seen to contain crystalline carvoxime. The last fraction and the tube of the

condenser are rinsed back into the flask with hot water; when cold, the solid carboxime is filtered off and drained by aid of a filter pump, and finally dried in the air. Should any oxime separate from the previous fractions of the distillate during the next day or so, it is added to the main quantity. The whole is then heated for an hour in a tared glass dish on the water-bath over an opening 43 mm. in diameter, and weighed; 0.100 gram is added, to correct for loss by volatilisation during the heating, and the sum is multiplied by 0.909, to calculate the equivalent amount of carvone. The error of the method amounts to several units per cent.; the influence on it of various modifications of the conditions of the experiment was investigated.

C. F. B.

Examination of Resins. X. Storax. By KARL DIETERICH (*Chem. Centr.*, 1899, ii, 541; from *Pharm. Centr.-Halle*, 40, 423—428, 439—443. Compare Abstr., 1898, ii, 58).—When testing storax, it is preferable to work on the crude sample instead of using the alcoholic extract.

To determine the acidity number, 1 gram of the sample is dissolved in 100 c.c. of cold 96 per cent. alcohol, and titrated with $N/2$ alcoholic potash, using phenolphthalein as indicator. The saponification number is found by dissolving 1 gram of the sample in 20 c.c. of $N/2$ alcoholic potash, and 50 c.c. of benzene, and, after 24 hours, titrating the excess of alkali with $N/2$ sulphuric acid. The following figures may be held to indicate the average composition of genuine storax: Water, not over 30 per cent.; ash, not over 1 per cent.; soluble in alcohol, not less than 60 per cent.; insoluble, not more than 3 per cent. Acidity number, 55—75; ether number, 35—75; saponification number, 100—140.

L. DE K.

Testing Storax. By FERD. EVERS (*Chem. Centr.*, 1899, ii, 594; from *Pharm. Zeit.*, 44, 592—593).—The author objects to Dieterich's proposal of applying tests to the crude resin (see preceding abstract).

L. DE K.

Examination of Resins. XI. Anime, Caranna, Dammar, Labdanum, Mastic, Sandarac, Tacamahaca, and Turpeth. By KARL DIETERICH (*Chem. Centr.*, 1899, ii, 541; from *Pharm. Centr.-Halle*, 40, 453—457).—A table giving the acidity, ether, and saponification numbers of the following resins: East and West Indian anime, caranna resin, several varieties of dammar, dammar adulterated with colophony, several varieties of mastic, labdanum, sandarac, tacamahaca resin, and turpeth resin. The acidity numbers of dammar and sandarac should be determined by dissolving 1 gram of the sample in 20 c.c. of $N/2$ alcoholic potash, adding 50 c.c. of benzene, and, after 24 hours, titrating the excess of alkali with $N/2$ sulphuric acid.

L. DE K.

Examination of Resins. XII. Ammoniacum, Bdellium, Galbanum, Opoponax and Sagapenum. By KARL DIETERICH (*Chem. Centr.*, 1899, ii, 542—543; from *Pharm. Centr.-Halle*, 40, 467—471).—A table showing the acidity, ether, and saponification

numbers of gum ammoniacum, bdellium, galbanum, opoponax, and sagapenum.

The acidity numbers of ammoniacum and galbanum are obtained by boiling 1 gram of the finely powdered sample with 50 grams of water and 100 grams of alcohol for 15 minutes in a reflux apparatus, 75 grams of the filtrate are then mixed with 10 c.c. of $N/2$ alcoholic potash, and after waiting for 5 minutes, the excess of alkali is titrated with $N/2$ sulphuric acid. The saponification number is found by using the author's cold benzene process.

The other resins are treated as follows: 1 gram of the sample is heated for 15 minutes with 30 c.c. of water, 50 c.c. of alcohol are added and the boiling continued for the same time; the liquid is then at once titrated with $N/2$ alcoholic potash. The saponification numbers are found by boiling 1 gram of the sample first with 30 c.c. of water and then adding 25 c.c. of $N/2$ alcoholic potash, the excess of which is afterwards titrated.

L. DE K.

Detection of "Saccharin" in Beer. By R. RÖSSING (*Chem. Centr.*, 1899, ii, 274; from *Zeit. öffentl. Chem.*, 5, 207—208).—The beer is acidified with phosphoric acid and shaken with an equal bulk of ether. The residue left on evaporating the ethereal extract is mixed with a little sand, dried in the water-oven, the powdered mass extracted with absolute ether, and an equal volume of benzene is added. The filtrate is then evaporated on a watch glass and the residue dried over sulphuric acid. The "saccharin" is thus obtained in white crystals of characteristic sweet taste.

L. DE K.

Colour Reaction for the Detection of Benzidine and Tolidine. By JULES WOLFF (*Chem. Centr.*, 1899, ii, 569; from *Ann. chim. anal. appl.*, 4, 263—264).—The substance is dissolved in a little glacial acetic acid, the liquid diluted with water, and lead dioxide suspended in water added; a splendid blue coloration is developed which is permanent in the cold. If other organic acids are used, the colour is not so intense. With a small amount of bromine, a blue coloration forms, but with excess a blue precipitate is obtained. Mineral acids prevent the reaction with either lead dioxide or bromine.

L. DE K.

Simple Alkalimetric Method for the Estimation of Salt-forming Alkaloids with the Aid of Phenolphthalein as Indicator. By HARRY M. GORDIN (*Pharm. Archives*, 1899, 2, 313—318, and *Ber.*, 1899, 32, 2871—2876).—The periodides (Abstr., 1899, i, 89) or mercuriodides (Prescott, Abstr., 1882, 664) of alkaloids, precipitated respectively by Wagner's and by Mayer's reagent, contain an indefinite amount of iodine or mercuric iodide, but apparently always a definite amount of hydrogen iodide, as represented by the formula, $m\text{Alk.}, \text{HI} + n\text{I}$, or $m\text{Alk.}, \text{HI} + n\text{HgI}_2$. This fact may be utilised for the estimation of alkaloids by titration. About 0.2 gram of anhydrous morphine is dissolved in 30 c.c. of standard hydrochloric acid (about $N/20$) in a 100 c.c. flask, Wagner's reagent (containing about 1 per cent. of free iodine and $1\frac{1}{2}$ of potassium iodide) added

gradually, the whole being shaken well after each addition, until further addition produces no further precipitate, when the contents are diluted to 100 c.c. and again shaken well. After the precipitate has settled thoroughly the liquid is filtered, 50 c.c. of the red filtrate decolorised by the gradual addition of 10 per cent. sodium thiosulphate solution, a few drops of phenolphthalein added, and the excess of acid titrated with *N*/20 potassium hydroxide. It is found that 1 c.c. of the acid is removed by 0.0137 gram of morphine; the equivalent quantities are, of hydrastine, 0.0184; strychnine, 0.0160; caffeine cryst., 0.0102; cocaine, 0.0146, and atropine 0.0139 gram. These alkaloids were then estimated in the same way, the factors just quoted being used in the calculation; the amounts found differed by about 1 per cent. only from those taken. Of Mayer's and Wagner's reagents that one is used which effects the more complete precipitation; if they are equal in this respect, Mayer's reagent is to be preferred, as the precipitate it produces settles more easily; when it is used, too, the subsequent addition of thiosulphate is unnecessary. Caffeine requires 50 c.c. of acid; colchicine cannot be estimated by this method, nor can berberine, which does not carry down any acid.

C. F. B.

Alkaloid resembling Aconitine found in a Corpse. By MECKE (*Chem. Centr.*, 1899, ii, 256—257; from *Zeit. öffentl. Chem.*, 5, 204—206. Compare *Abstr.*, 1899, 311).—A ptomaine with properties very similar to those of aconitine has been found in a corpse. This alkaloid is extracted from alkaline solutions by ether, and gives the general reactions of the alkaloids, forming with phosphotungstic acid a white, with phosphomolybdic acid a yellow, and with a solution of iodine in potassium iodide a brownish precipitate. It gives a faint turbidity with mercuric chloride, and with concentrated sulphuric acid it forms, after a time, a reddish-violet coloration, which changes to a darker shade on warming. It remains colourless with dilute sulphuric or phosphoric acid, but becomes violet on evaporating. The yellowish solution in nitric acid, when evaporated, leaves a yellow residue which turns orange when moistened with potassium hydroxide solution. Even very small quantities instantly reduce potassium ferricyanide, and with Fröhde's reagent the alkaloid gives a greenish coloration, changing to yellowish-brown on warming. It is not precipitated by tannic acid, and after adding bromine water it is not attacked by concentrated sulphuric acid; potassium dichromate has also no action on it.

The violet coloration obtained by treating aconitine with phosphoric acid or concentrated or dilute sulphuric acid is only slowly formed, and differs from that of the corpse alkaloid both in shade and intensity. Delphinine, although stated by Otto to give a violet coloration with phosphoric acid, was found to produce only a brownish coloration, and its behaviour with sulphuric acid and bromine is not like that of the ptomaine.

The present methods of testing for aconitine are only to be trusted when considerable quantities are present and decomposed animal matter absent. Hilger and Tamba's reaction with phosphoric acid is

not available in presence of ptomaines, and, moreover, is scarcely characteristic of aconitine, for the different commercial varieties give different reactions. Urine which is several days old, when evaporated with phosphoric acid, also gives the same violet coloration as aconitine. The reactions with concentrated sulphuric acid, potassium ferricyanide (Brouardel-Boutmy's reaction), and Fröhde's reagent are also untrustworthy. According to Jürgens, characteristic crystals of aconitine potassium iodide are obtained by dissolving the alkaloid in a drop of dilute acetic acid, evaporating with a grain of potassium iodide, and washing with water, but in many cases this test gave only amorphous precipitates or the tabular crystals of pseudoaconitine.

E. W. W.

Delicate Test for Caffeine. By ANDREA ARCHETTI (*Chem. Centr.*, 1899, ii, 453; from *Boll. Chim. Farm.*, 38, 340—341).—A solution of potassium ferricyanide is mixed with half its volume of nitric acid and heated to boiling. On adding an aqueous solution of caffeine a deposit of prussian blue will be noticed. The reaction is also given by other xanthine bases and uric acid, but only very feebly.

L. DE K.

Estimation of Cornutine. By FRANZ MUSSET (*Chem. Centr.*, 1899, ii, 323; from *Pharm. Centr.-Halle*, 40, 396).—The ethereal solution obtained according to Keller's directions contains, besides the cornutine, a resinous matter causing high result. By treating the weighed residue repeatedly with water containing 0.5 per cent. of hydrogen chloride, the cornutine dissolves and the insoluble resin may be weighed and allowed for.

L. DE K.

Recognition of Morphine and its Derivatives. By RUDOLF ROBERT (*Chem. Centr.*, 1899, ii, 149—150; from *Sonderabdruck aus Apoth.-Zeit.*, 14, No. 37).—The reagent proposed by the author's pupil Marquis is prepared by mixing 2—3 drops of formaldehyde solution with 3 c.c. of concentrated sulphuric acid. The pulverised alkaloid is added to this in a porcelain basin. *Morphine* gives at first a purple-red, passing through violet to almost pure blue; if partially protected from the air by placing in a test-tube, the blue colour remains for a long time. *Dionine* gives a deep blue, *codeine* a violet, *heroine* a reddish-violet turning to bluish-violet, *peronine*, a permanent reddish-violet, *methylphenomorpholine* an intense red. The absorption spectra of these coloured solutions show small differences.

M. J. S.

Estimation of Chloral Hydrate and Morphine in Organs. By RUSSWURM (*Chem. Centr.*, 1899, ii, 794; from *Pharm. Centr.-Halle*, 40, 543—544).—The united distillates from an acid and an alkaline distillation, containing therefore both chloral hydrate and chloroform, is diluted with alcohol to a definite bulk, and the chlorine estimated by boiling an aliquot part with alcoholic potash in a reflux apparatus, neutralising with nitric acid, and titrating with silver nitrate.

Morphine is estimated by first extracting the ammoniacal solution with hot amyl alcohol, which is, in turn, shaken with dilute hydrochloric acid. According to the author, the alkaloid may now be

obtained by supersaturating the liquid with ammonia and agitating with chloroform; this is then concentrated to a few c.c. in a small weighed beaker, and the morphine completely precipitated by adding 50 c.c. of light petroleum of low boiling point. L. DE K.

Estimation of Santonin in the Flower Buds of *Artemisia Maritima*. By KARL THAETER (*Arch. Pharm.*, 1899, 237, 626—632).—The author defends his method (*Abstr.*, 1898, ii, 59) against Katz's criticisms (*Arch. Pharm.*, 1899, 237, 245). The extraction with ether must be continued for 12—18 hours. Before the magnesia is added, the solution should be evaporated to dryness, and the residue powdered; after mixture, the whole is moistened evenly with water and dried as rapidly as possible; there is then little fear that any of the santonin will be converted into magnesium salt. C. F. B.

Estimation of Urinary Indican. By EYVIN WANG (*Zeit. physiol. Chem.*, 1899, 23, 576—584. Compare *Abstr.*, 1898, ii, 659; 1899, ii, 458).—The author defends his method against the criticisms of Bouma (*Abstr.*, 1899, ii, 568). He holds that the method of purification described is necessary and correct, for the reddish-brown pigment removable by alcohol does not originate from indigo. W. D. H.

Volumetric Estimation of Sodium Cacodylate. By HENRI IMBERT and A. ASTRUC (*J. Pharm.*, 1899, [vi], 10, 392—395).—Cacodylic acid is neutral to methyl-orange, but behaves as a monobasic acid towards phenolphthalein, whereas pure sodium cacodylate is alkaline to methyl-orange and neutral to phenolphthalein. The commercial salt, however, is always acid to phenolphthalein, due to the presence of free acid. 1.6 grams of sodium cacodylate are dissolved in 100 c.c. water and to 10 c.c. of this solution carefully neutralised, using phenolphthalein as indicator, decinormal hydrochloric acid or sulphuric acid is then added until the liquid is neutral to methyl-orange. The number of c.c. of acid required multiplied by ten gives the percentage of pure sodium cacodylate. H. R. LE S.

Separation of Proteids from Flesh-bases by means of Chlorine and Bromine. By HARVEY W. WILEY (*Chem. Centr.*, 1899, ii, 586; from *Chem. News*, 80, 88—89).—The freshly powdered dry material, from which the fat has been removed by ether, is first extracted with cold and then with hot water and the extract filtered. The amount of proteids insoluble in water is calculated by multiplying the difference between the amount of nitrogen in the original material and that in the insoluble portion by 6.25. The filtrate, after acidifying with hydrochloric acid, is oxidised by repeatedly shaking with bromine. After remaining over night, the precipitated proteids are filtered and washed with water. The amount of flesh bases is obtained by multiplying the difference between the total amount of nitrogen and the sum of the amount of nitrogen in the soluble and in the insoluble proteids by 3.12. Liebig's extract was found by this method to contain 8.92 per cent. of proteids, previous determinations having given lower results. E. W. W.

Source of Error in Testing for Albumin in Urine. By E. DERODE and OUI (*Chem. Centr.*, 1899, ii, 570; from *Ann. chim. anal. appl.*, 4, 261—262).—Before being tested for albumin, the urine, if not quite clear, should be filtered; if, however, the turbidity is caused by micro-organisms, the ordinary filter fails and a so-called Kitasato filter must be employed.

It has been proposed to clarify the urine by means of calcined magnesia, but the authors find that this also precipitates most of the albumin.
L. DE K.

Microchemistry of Crystalline Hæmatin Compounds. Detection of Blood. By CASIMIR STRZYZOWSKI (*Chem. Centr.*, 1899, ii, 140, 225; from *Oesterr. Chem. Zeit.*, 1899, 2, 305, 333—335).—Largely a repetition of earlier work. Ox-blood freed from salts, cholesterol, and fat was employed. None of Husson's results can be confirmed, except those relating to the formation of bromine and iodine compounds of hæmatin. Axenberg's mercury and manganese hæmatin compounds are non-existent. Buffalini's method (*Abstr.*, 1886, 184) must also be rejected, since the halogens (iodine, however, the least) destroy the colouring matter of blood. The results obtained by Bikfalvi (*Abstr.*, 1887, 165) by adding acetic acid and a haloid salt of an alkali metal to dialysed blood, appear to be perfectly correct. The so-called hæmidin crystals obtained by Dannenberg and others (*Abstr.*, 1887, 408) are nothing but sulphur. Teichmann's method simplified as follows will detect 0.000025 gram of blood. To the dried substance on a microscope slide with cover, acetic acid mixed with 1/50 vol. of hydriodic acid is added and the object is heated for a short time; well formed black crystals are obtained. Another very sensitive reagent is a mixture of 10 c.c. of glycerol of sp. gr. 1.26 with 2—3 drops of concentrated sulphuric acid. Blood, when heated with a very small quantity of this reagent on an object glass and examined with a magnifying power of 400 diameters, shows small, dark needles of hæmatin sulphate.
M. J. S.

Detection of Yolk of Egg in Margarine. By MECKE (*Chem. Centr.*, 1899, ii, 321—322; from *Zeit. öffentl. Chem.*, 5, 231—232).—Margarine melted at 45° is shaken with half its volume of a 1 per cent. solution of salt. The aqueous liquid is freed from fat by agitating with light petroleum and then cleared by alumina-cream. The filtrate is diluted with 5 times its bulk of water, when if yolk of egg is present in the sample, an abundant, flocculent precipitate of vitellin will be obtained. Or the margarine may be dissolved in light petroleum, the undissolved matter washed with ether, and then treated with salt solution.
L. DE K.

Detection of Albumoses in Urine. By LUDWIG VON ÁLDOR (*Chem. Centr.*, 1899, ii, 728—729; from *Berl. Klin. Woch.*, 36, 764—767, 785—787).—Any albumin is first removed by precipitation with trichloroacetic acid. 6—10 c.c. of the urine are acidified with 1—2 drops of hydrochloric acid and precipitated with slight excess of 5 per cent. solution of phosphotungstic acid. The precipitate is repeatedly whirled in a centrifugal apparatus with absolute alcohol

until all colouring matter is extracted and then suspended in water and mixed with aqueous sodium hydroxide. A blue coloration is noticed, which, however, fades on exposure to the air; the colourless liquid is then treated, as usual, with copper sulphate. L. DE K.

Analysis of Rubber Wares. By ROBERT HENRIQUES (*Zeit. angew. Chem.*, 1899, 802—804. Compare Abstr., 1893, ii, 399, and 1895, ii, 96, 191).—*Estimation of the total Sulphur and Metals.* The process does not materially differ from the former one, being carried out by oxidising with nitric acid, neutralising with excess of soda, and fusing the dry mass; the aqueous solution of this will contain the sulphur as sodium sulphate, whilst the metallic compounds remain as oxides or carbonates in the insoluble residue. For the detection and estimation of vermilion, which is often present in small quantities, the substance is digested with nitric acid, which gradually decomposes and dissolves the mercury sulphide; after expelling the bulk of the acid and diluting with water, the liquid is precipitated with hydrogen sulphide and the mercury looked for in the metallic sulphides so obtained.

Estimation of "Faktis" in Vulcanised Wares.—It is now recommended that the mass which has been exhausted with alkali shall be removed from the filter before drying to constant weight.

Estimation of Unsaponifiable Oils in Vulcanised Wares.—The mass, after being extracted with alkali, dried, and weighed, is again extracted with ether, the loss in weight representing the unsaponifiable matter, such as rosin-oil, paraffin, &c.

Estimation of "Faktis" in Non-vulcanised Wares.—The old process was not always satisfactory, and the following method has been substituted for it: 5 grams of the rasped sample is covered with 25 c.c. of benzene and heated on a boiling water-bath for an hour, the Erlenmeyer flask being attached to a reflux condenser; the whole is then left over night. The mass may now be successfully attacked by alcoholic soda.

Estimation of Unsaponifiable Oils in Non-vulcanised Wares.—Boiling acetone is substituted for ether and after evaporating the solvent, the residual unsaponifiable matter is weighed.

Estimation of Carbonic Anhydride.—Attention is called to the importance of estimating the carbonic anhydride present in combination with calcium, lead, zinc, &c. When dealing with non-vulcanised wares, the sample should first be repeatedly extracted with boiling nitrobenzene to remove the bulk of the rubber so as to facilitate the action of acids. L. DE K.

General and Physical Chemistry.

Indices of Refraction of Metals. By EDMOND VAN AUBEL (*Zeit. physikal. Chem.*, 1899, 30, 565—566).—A comparison of the indices of refraction of metals obtained by calculation from the molecular refraction of salt solutions with those obtained directly by Drude (*Ann. Phys. Chem.*, 1890, [ii], 37, 537). The values show fair agreement in some cases, but in others are of a different order of magnitude, for example, silver, 2.37 and 0.203. Kundt's law, which states that the product of the index of refraction and electrical conductivity is constant, does not hold for either the direct or calculated values.

L. M. J.

Colour Changes of Illuminated Substances. By HEINRICH BILTZ (*Zeit. physikal. Chem.*, 1899, 30, 527—528).—Marckwald has given an account of these changes to which he has applied the term 'phototropy' (this vol., ii, 2). To the sensitive compounds there mentioned may be added the hydrazone of benzaldehyde and cumilinosazone, anisilosazone, and piperilosazone. These compounds are yellow or greyish-yellow, but on exposure to light become red or orange in about an hour, returning again to the original colour in the dark. Benzilosazone, salicylosazone, and vanillylosazone are, however, not phototropic.

L. M. J.

Chemical Effects produced by Becquerel Rays. By P. CURIE and SKŁODOWSKA CURIE (*Compt. rend.*, 1899, 129, 823—825).—The radiations from highly radio-active barium salts convert atmospheric oxygen into ozone, and the latter is readily detected in the air of closed flasks containing the radio-active compounds. The compounds producing this result are all luminescent and highly radio-active, but their effect on oxygen seems to be connected with radio-activity rather than with luminescence.

The radiations also affect glass, and the vessels containing the salts gradually become deep violet and almost black, especially where the glass is in contact with the salt, even if the glass does not contain lead. The intensity of the coloration and the time required for its production depend on the intensity of the radio-activity.

Barium platinocyanide, under the influence of these radiations, becomes dark coloured and less fluorescent, but regains its original colour when exposed to sunlight, and at the same time becomes phosphorescent. Villard has obtained similar results with Röntgen rays (compare also Giesel, *Ann. Phys. Chem.*, 1899, [ii], 69, 91).

C. H. B.

Chemical Action of the X-Rays. By P. VILLARD (*Compt. rend.*, 1899, 129, 882—883. Compare preceding abstract).—The darkening of the wall of a Crookes' tube, which has been working for some time, is due to the reduction of the lead present in the glass to the metallic state by the cathode rays. If these are cut off by a thin

sheet of aluminium, which is transparent to the X-rays, the glass is coloured violet. This is due to the oxidising action of the X-rays, and the coloration is no doubt due to the manganese present in the glass.

H. R. LE S.

Phosphorescence Phenomena produced by the Radiations from Radium. By HENRI BECQUEREL (*Compt. rend.*, 1899, 129, 912—917).—The author finds that, in general, substances which phosphoresce when exposed to the action of ultra-violet rays, or of the X-rays, also become luminous under the influence of the radiation emitted by radio-active barium chloride; the order of the relative intensities of the luminous effects is, however, not the same in the two cases.

The phosphorescence excited by radium in certain minerals shows great persistence; fluorite, for example, remains luminous 24 hours after the influence of the radium has ceased.

When phosphorescent substances, which have been heated and thus rendered incapable of phosphorescence, are subjected to the action of an electric spark or to the prolonged action of the violet and ultra-violet rays, they are found to possess the property of exhibiting phosphorescence on heating. Fluorite, in these circumstances, emits a greenish-blue light, and the author finds that this mineral, after heating and exposing it to the radium radiation, gives out when heated a greenish-blue light which spectroscopic analysis shows to be identical with that produced by the electric spark.

T. H. P.

Influence of the Magnetic Field on the Rays Emitted by Radio-active Substances. By HENRI BECQUEREL (*Compt. rend.*, 1899, 129, 996—1001).—The radio-active substance used was barium chloride, and the influence of the magnetic field on the rays emitted by it was investigated by means of a fluorescent screen or a photographic plate. The author confirms the observations of Meyer and von Schweidler (*Physikalische Zeitschrift*, No. 10, 113—114) that some of the rays follow the direction of the magnetic field and are undeflected, whereas those in a plane at right angles to the magnetic field are deflected.

The results obtained point to a close relationship between cathodic rays and the rays emitted by radio-active substances. H. R. LE S.

Radiation of Radio-active Substances. By HENRI BECQUEREL (*Compt. rend.*, 1899, 129, 1205—1207). **Action of the Magnetic Field on Becquerel Rays: Deflected and Undeflected Rays.** By P. CURIE (*Compt. rend.*, 1900, 130, 73—76). **Penetration of Undeflected Becquerel Rays.** By SKŁODOWSKA CURIE (*Compt. rend.*, 1900, 130, 76—79).—The rays emitted by a very active specimen of Curie's polonium are not deflected in the magnetic field; the experiments were made about a month after the preparation of the substances, and the results are contrary to those obtained by Giesel with freshly prepared polonium compounds (this vol., ii, 19).

A portion of the rays emitted by radium are deflected by the electro-magnet; these behave like Röntgen rays, their velocity is of the same order, and their penetrating power increases with the thickness of the absorbent layer; the undeflected rays correspond with those from

polonium, and their penetrating power varies in the opposite sense to that of the deflected rays. G. T. M.

Electromotive Behaviour of Chromium. By WILHELM HITTOFF (*Zeit. physikal. Chem.*, 1899, 30, 481—507).—The peculiarities in the electromotive behaviour of chromium are further investigated (compare Abstr., 1898, ii, 363), and the author advances many arguments in support of the view that the inactive state cannot be due to the formation of a film of oxide. Owing to the existence of the different classes of chromium compounds, the metal may exhibit any potential between the two extreme values; the highest value corresponds with the active state in which chromium gives rise to the lower compounds. This active state is assumed when the metal is placed in sulphuric, oxalic, hydrofluosilicic, or the halogen acids, at temperatures which are lower the more concentrated the acid; it is also active in fused halogen salts or in their boiling solutions. The metal becomes inactive when immersed in solutions containing free chlorine or bromine, or in strong oxidising agents. The limiting values, however, last but a short time after removal from the liquids, the metal speedily assuming an intermediate state; the most stable active state is that produced by fused halogen salts. The activity is also lowered in all cases when the metal serves as an anode for a current produced either externally or internally, and, with sufficiently strong currents, chromic acid is produced, either by decomposition of water by anion and subsequent union of the metal and oxygen, or by the intermediate formation of a compound of the anion and chromium. When the metal is used as a cathode, it rapidly assumes the active state. The author points out that Berzelius and Wöhler had previously observed differences in chromium under different conditions. L. M. J.

Influence of the Addition of a Salt with one similar Ion on Electromotive Force and Diffusion Velocity. By RICHARD ABEGB and EMIL BOSE (*Zeit. physikal. Chem.*, 1899, 30, 545—555).—A theoretical investigation of the above question. It is shown that if u and v are the cation and anion velocities, the addition of a salt with a similar cation or anion causes change of velocity of diffusion, tending to the values $V. (u + v)/2v$ or $V. (u + v)/2u$ respectively. In acids, the cation has a velocity about six times that of the anion, whilst in bases the velocity of the OH anion is about three times that of the cation. The velocity of diffusion of an acid or of a base hence is greatly increased by the addition of one of its neutral salts, and experiments are recorded in verification of this. Similarly, owing to the slight velocity of MnO_4^- and CrO_4^{2-} ions, the diffusion of potassium permanganate or potassium chromate is decreased by the addition of potassium chloride. The increase of the catalytic action of an acid caused by the addition of its salts may be due to the increased mobility of the hydrogen ion. L. M. J.

Molecular Susceptibility of the Salts of the Rare Earths. By H. DU BOIS and OTTO LIEBKNECHT (*Ber.*, 1899, 32, 3344—3348).—In determining the molecular susceptibility of a paramagnetic salt,

the substance is added to water until its paramagnetism just counterbalances the diamagnetism of the solvent; when this is the case, the meniscus of a portion of the solution contained in a capillary tube placed between the poles of an annular electromagnet remains stationary, whereas it moves backwards or forwards if the solution is either para- or dia-magnetic. The molecular susceptibility of the salt is then calculated from the equation $i_m = -m.M_w/M_s.x$ where m is the molecular weight of salt, M_w/M_s the ratio between the weights of water and salt in the non-magnetic solution, and x the specific susceptibility of water at 18° ; the exact value of this constant is not known, and the number 0.75×10^{-6} is employed as an approximation; the results, however, may be expressed in the form $-i_m/x$, and this expression is independent of the constant. The results obtained with the salts of eight of the rare earths are tabulated in the following manner:

	Salt, RCl_3 .	Atom. wt. (O=16).	Mol. wt. m .	$\frac{M_w}{M_s}$.	$-\frac{i_m}{x}$.	i_m .
1.	Yttrium chloride	89.0	195.35	1.41	276	0.00021
2.	{ Cerium „	140.0	246.35	13.197	3250	0.00243
	{ „ bromide „	„	379.88	8.4398	3210	0.00240
3.	Praseodymium chloride. 140.4	246.75	17.72	4370	0.00328	
4.	{ Neodymium „ „	143.6	249.95	27.995	7000	0.00525
	{ „ nitrate.....	„	329.72	20.98	6920	0.00519
5.	Samarium chloride	150	256.35	60.52	15510	0.01164
6.	Gadolinium „	156	262.35	130.24	34170	0.02563
7.	Erbium „	166	272.35	179.59	48910	0.03668
8.	Ytterbium „	173	279.35	33.95	9480	0.00711

These figures show that the salts investigated are derived from a well-defined group of paramagnetic elements, corresponding with the group chromium, manganese, iron, cobalt, nickel, and copper. In both cases, it is found that when the elements are arranged in the order of their atomic weights, the susceptibility is least for the salt of lowest atomic weight, also that it rises to a maximum, and then falls again. In the chromium-copper group, the maximum is reached at the third member (iron); cobalt is more paramagnetic than nickel, although recent atomic weight determinations place the latter nearer to iron. In the rare earth group, the maximum is reached only at the seventh stage (erbium), and then drops suddenly to ytterbium; in this group the increase and decrease of paramagnetism is strictly in accordance with the ascending order of the atomic weights.

G. T. M.

Change of Thermal Conductivity during Melting. By EDMOND VAN AUBEL (*Zeit. physikal. Chem.*, 1899, 30, 563—564).—The results of Lees (*Phil. Trans.*, 1898, 191, 428) have shown that fusion is not necessarily accompanied by a sudden change of conductivity. In the case of water, however, the conductivity at 0° is 0.072 and in the solid state between -21° and 0° about 0.30, so that, most probably, a sudden change occurs during the melting of ice.

L. M. J.

Influence of Pressure on the Critical Temperature of Complete Mixture. By N. J. VAN DER LEE (*Proc. K. Akad. Wetensch. Amsterdam*, 1898, 1, 158—165).—For two liquids, only partly soluble in each other, there exists a temperature above which mixture in all proportions is possible. The influence of pressure on this phenomenon has been investigated for mixtures of water and phenol, the critical temperature of complete mixture being in this case about 67° . The mixture to be investigated was contained in a thick glass tube of small bore, and subjected to pressures of 1—180 atmospheres; an electromagnetic stirring apparatus secured thorough mixing of the components in the tube. By means of a thermostat, in which ethyl alcohol boiled under varying pressures, the mixture could be kept at the desired temperature.

The temperature of complete mixture was in all cases found to rise slightly with increase of pressure; thus, in a case where 34 per cent. of phenol was present, the temperature of complete mixture was 67.6° under a pressure of 1 atmosphere, and 68.1° under a pressure of 130 atmospheres. The temperature of complete mixture was highest for the composition just referred to.

Theoretical considerations point to the curve $p=f(x)$, connecting the composition and pressure of the saturated vapour of the mixture, having a maximum or minimum when there is 34 per cent. of phenol present. The vapour pressures of numerous mixtures of water and phenol have accordingly been determined for the temperature range 71 — 90° . The composition of the mixture with maximum vapour pressure for any given temperature, cannot be exactly determined from the numbers obtained, but it is close to 34 per cent. of phenol.

J. C. P.

Hydrate of Sodium Dioxide and Preparation of Hydrogen Peroxide. By ROBERT DE FORCRAND (*Compt. rend.*, 1899, 129, 1246—1249).—The heat of dissolution of the hydrate $\text{Na}_2\text{O}_2 \cdot 8\text{H}_2\text{O}$ is -14.868 Cal.; its heat of formation from sodium dioxide and water is 34.081 Cal., and from the dioxide and ice, 22.641 Cals. These values indicate that the hydrate is possessed of considerable stability, and on this account it may be employed in the preparation of hydrogen peroxide; it furnishes a strong solution of this compound when dissolved in cold hydrochloric acid. The reaction Na_2O diss. + H_2O_2 diss. = Na_2O_2 diss. is accompanied by an evolution of 4.713 Cals. For the solid substances, the stable condition is Na_2O_2 , for 27.755 Cals. are evolved during the combination of oxygen with solid Na_2O ; in solution, the stable condition is $\text{Na}_2\text{O} + \text{O}$, for the addition of oxygen to dissolved Na_2O is attended by an absorption of heat equal to -16.987 Cals.

G. T. M.

Compound Metallic Radicles: Mercury Derivatives. By MARCELLIN P. E. BERTHELOT (*Compt. rend.*, 1899, 129, 918—920).—The following heats of combustion and formation have been determined:

	Combustion.		Formation.
	At const. vol.	At const. press.	
Mercurydimethyl (liq.)	430·8 cal.	431·8 cal.	—36·2 cal.
Mercurydiethyl (liq.)	733·6 „	735·0 „	—12·8 „
Mercurydiphenyl (cryst.) ...	1563·8 „	1565·3 „	—88·5 „

T. H. P.

Compounds of Lithium Chloride with Ethylamine. By J. BONNEFOI (*Compt. rend.*, 1899, 129, 1257—1259).—The compound, $\text{LiCl} \cdot \text{NH}_2\text{Et}$, produced when ethylamine is passed over lithium chloride heated above 70° , is a white, porous substance the heat of dissolution of which in water is 7·503 Cal.; its heat of formation determined experimentally is 13·834 Cal., the value calculated by Clapeyron's formula being 13·717 Cal. The substance closely resembles the corresponding methylamine and ammonia compounds the heats of formation of which are respectively 13·820 and 11·842 Cals. (Abstr., 1897, ii, 371; 1899, ii, 96). The compound $\text{LiCl} \cdot 2\text{NH}_2\text{Et}$ is formed at temperatures between 58° and 70° ; the heat of dissolution is 9·43 Cal. and the heat of formation is 24·817 Cal. The heat evolved by the fixation of the second molecule of the amine calculated from the dissociation pressures of the substance by Clapeyron's formula is 11·09 Cal. The compound $\text{LiCl} \cdot 3\text{NH}_2\text{Et}$ is obtained below 58° , and even when the liquid amine was employed no further combination took place; the heat of dissolution is 11·77 Cal. and the heat of formation 35·387 Cal. The heat evolved during the fixation of the third molecule of the amine is 10·57 Cal. determined calorimetrically, and 10·503 Cal. calculated by Clapeyron's formula from the dissociation pressures.

G. T. M.

Lactic Acid. By MARCELLIN P. E. BERTHELOT and MARCEL DELÉPINE (*Compt. rend.*, 1899, 129, 920—926).—Thermochemical data for silver and zinc lactates and for lactide are given in the following table:

	Heat of combustion			Heat of	
	1 gram.	1 mol. at const. vol.	1 mol. at const. press.	formation from elements.	solution.
$\text{C}_3\text{H}_5\text{O}_3\text{Ag}$	1609·7 cal.	316·6 Cal.	316·5 Cal.	138·9 Cal.	—2·05 Cal.
$(\text{C}_3\text{H}_5\text{O}_3)_2\text{Zn}$...	2592·1 „	640·15 „	640·15 „	355·45 „	+8·00 „
$\text{C}_3\text{H}_4\text{O}_2$	4542·8 „	327·1 „	327·1 „	93·8 „	+2·10 „

The heats of neutralisation of lactic acid are: with $\frac{1}{2}\text{Ag}_2\text{O}$, 4·1 Cal.; with $\frac{1}{2}\text{ZnO}$ (hydrated), +9·95 Cal.; and with $\frac{1}{2}\text{ZnO}$ (anhyd.) +9·3 Cal.

These numbers give, for the heat of formation of lactic acid from its elements, mean values of 163·2 Cal. for the pure liquid acid and 164·3 Cal. for the dissolved acid.

T. H. P.

Heats of Fractional Neutralisation of Carbonylhydroferrocyanic Acid compared with those of Hydroferrocyanic Acid. By JOSEPH A. MULLER (*Compt. rend.*, 1899, 129, 962—964).—Each addition of one-fourth of the equivalent quantity of potash to a

dilute solution of a gram-mol. of hydroferrocyanic acid gives a heat development of almost exactly 14 Cals., the total at 18.6° being 56.18 Cals. Sensibly the same number of Cals. (14) are liberated when carbonylhydroferrocyanic acid is neutralised by thirds in dilute solution, the mean total heat evolutions being, at 19.4° with potash, 41.91 Cals., and at about 18° with baryta, 42.29 Cals.

Thus, carbonylhydroferrocyanic acid is a strong acid, and the replacement of HCN in the molecule of hydroferrocyanic acid by the carbonyl group has no appreciable influence on the acidic properties of the remaining hydrogen atoms. T. H. P.

Narceine. By ÉMILE LEROY (*Compt. rend.*, 1899, 129, 1259—1261).—The heat of hydration of narceine is 6 Cal. for the dihydrated form, and, in addition, 3 Cal. are evolved when this is converted into the trihydrate. The heat of combustion is 2790.9 cal. at constant volume, and 2792.2 cal. at constant pressure. The heat of formation of the anhydrous base is 302.2 Cal., that of the dihydrate being 308.24 Cal. The heat of neutralisation of the dihydrated form in excess of hydrochloric acid is -4.62 Cal., whilst that of the anhydrous base is 1.58 Cal. The hydrochloride, $C_{23}H_{27}O_8N.HCl$, crystallises, with $3H_2O$, from a solution containing excess of acid; the heat of hydration of the salt is 6.76 Cal. with water, and 2.08 Cal. with ice, the heat of formation of the anhydrous salt being 21.52 Cal. The heat of formation of the potassium derivative, $C_{23}H_{26}O_8NK$, is 16.7 Cal., the heat evolved on adding potassium hydroxide solution to an aqueous solution of the alkaloid being 11.5 Cal.

Narceine is the least basic of the opium alkaloids, and, like narcotine, is neutral to litmus; the heat of formation of the potassium derivative indicates a distinctly acidic function, the substance being intermediate in stability between the acetates or benzoates and the phenoxides. G. T. M.

Fractional Distillation under Reduced Pressure. By GIUSEPPI ODDO (*Gazzetta*, 1899, 29, ii, 355—357).—The apparatus described consists of a T-piece fitted to the end of the condenser by means of a piece of rubber tubing which is slightly greased so as to allow of the T-piece being rotated. To the two branches of the latter are fitted two receivers, one being an ordinary flask, and the other an Erlenmeyer flask which is also in connection with the pump used for exhaustion. After the first fraction has been collected in one of these receivers, the T-piece is turned round so that the second receiver comes into use. If more than two fractions are required, to each branch of the T-piece another T-piece is fitted by means of a piece of greased rubber tubing; in this way, four fractions are obtainable. T. H. P.

Determination of Freezing Points in Dilute Solutions. By MEYER WILDERMANN (*Zeit. physikal. Chem.*, 1899, 30, 508—526).—A consideration of the errors which must exist in thermometric determinations of freezing points. The formation of ice caps and nets is probably due to the presence of variable quantities of air and organic compounds in the water; these impurities also, although not indicated by the conductivity, may occasion variations of the freezing point, to

the extent of a few thousandths of a degree. Changes of external and internal pressure may also cause errors, the variation of the observed freezing point with the author's $1/1000^{\circ}$ thermometer being about 0.0003° per mm. of mercury. For accurate work also, the thermometer should be always kept at a temperature approximately equal to zero and not at the ordinary temperature. The effect of variations in the external temperature is also considered, but a more subtle source of error lies in the existence in the thermometer of rough places and dead points, which the mercury is unable to pass when the actual temperature is sufficiently near. Errors are also introduced owing to inaccuracies of calibration, and accuracy is hence frequently expected beyond that possible; for example, if an accuracy of 0.0001° is required with a $1/100^{\circ}$ thermometer, then the calibration should be performed with a mercury thread of about 1 mm. in length. Other errors not due to causes inherent in the method are also considered, and the author replies briefly to criticisms on his work, (compare Abstr., 1896, i, 352, 587). L. M. J.

Freezing Points of Mixed Crystals of Two Compounds. By H. W. BAKHUIS ROOZEBOOM (*Zeit. physikal. Chem.*, 1899, 30, 385—412).—A theoretical consideration of the phenomena of solidification of mixed crystals under various conditions; the following types are considered. A. The liquid solidifies to a continuous series of mixed crystals; three different types of curves are obtained, namely, in the cases where (1) the freezing point for every mixture lies between those of the two constituents, (2) a maximum, and (3) a minimum occurs. Many examples of the first case have been examined; of the second, no case has been completely studied, but lead-thallium mixtures are probably an example, while the third type is exemplified by mixtures of mercuric bromide and iodide. The general law is deduced that in all cases the liquid phase is richer than the solid phase, in that constituent which, if added, causes a depression of the freezing point. B. When the mixed crystals form an interrupted series, two more types of curves result; (4) when the freezing point curve contains a transition point at which the two crystal mixtures occur together, whilst a maximum or minimum may also be present—an example of this type has been found in mixtures of sodium and silver nitrates; (5) an eutectic point occurs in the freezing point curve; examples are mixtures of thallium and lead nitrates (Van Eijk, next page), and also of naphthalene and monochloroacetic acid (Cady, Abstr., 1899, ii, 405). When two different classes of crystals result, new types of curves are obtained closely resembling 4 and 5, and the author discusses the means of determining the type of curve indicated by experimental determinations of the freezing point. The accounts of the experimental realisation of the various types mentioned in the paper are deferred. L. M. J.

Transition Points in Mixed Crystals. By H. W. BAKHUIS ROOZEBOOM (*Zeit. physikal. Chem.*, 1899, 30, 412—429).—The possible types of curves for the transition of one set of mixed crystals to another are considered; the following types occur:—(1) A continuous series of mixed crystals, α , change to a continuous series, β ; the

forms of curve are analogous to types 1, 2, 3 in the preceding abstract, a complication being, however, introduced when only one component undergoes a transition; an example is the transition of mixtures of mercuric bromide and iodide. (2) A continuous series, α , change to a discontinuous series, β ; the transition curves are here analogous to types 4 and 5 of the freezing point curve, an example is probably the mixture of azoxyanisole and azoxyphenetole (Abstr., 1898, ii, 286); in this case also, transition of only one component may occur. (3) The mixed crystals form in the α state, and in the β state a continuous series; examples are the systems potassium and sodium nitrates, and sodium and silver nitrates. (4) The mixed crystals form discontinuous series in both states, an example being potassium and thallium nitrates (following abstract). (5) Isodimorphous mixed crystals change into a continuous or (6) an interrupted series of mixed crystals. Further types may occur in which the isodimorphous crystals are discontinuous, but these are not considered. L. M. J.

Formation and Transition of Mixed Crystals of Potassium and Thallium Nitrates. By C. VAN EIJK (*Zeit. physikal. Chem.*, 1899, 30, 430—459).—The melting point and transition curves were completely examined in the case of mixed crystals of the above compounds. The melting points of the pure compounds are: potassium nitrate 339° , thallium nitrate 206° , and an eutectic point occurs at 182° , the mixture containing 31 per cent. of potassium nitrate; the law stated by Roozeboom (preceding abstracts) regarding the composition of the solid and liquid phases was verified. During the solidification of the mass, the composition of the liquid phase changes continuously and the temperature falls; if the freezing is sufficiently slow, it is probable that the composition of the solid would also change, *pari passu*, until the whole mass solidifies at a final temperature corresponding with that at which the solid of the given composition is in equilibrium with a liquid phase. In the experiments, however, the solid phase was not found to change sufficiently rapidly, so that the final temperature is always lower than that deduced, as above, from the curves. As products of the freezing, a continuous series of rhombohedra were obtained to 20 per cent., and a second continuous series from 50 to 100 per cent. of potassium nitrate; for intermediate values, a conglomerate of the mixed crystals is obtained. The transition temperatures were obtained by both thermometric and dilatometric methods, as well as by the microscopical examination of the crystals. It was found that change to rhombic crystals occurs at 129° for potassium nitrate, and at 144° for thallium nitrate. For the mixed crystals, continuous transition curves are obtained from 144° to 133° on the thallium side, and from 129° to 108.5° on the potassium side. The conglomerate has, however, two transition temperatures, the first at 133° , at which temperature it changes to a mixture of rhombohedra and rhombic crystals, and the second at 108.5° , where the remaining rhombohedra change to the rhombic form. Although no transition in the conglomerate occurs above 133° , the composition of the two sets of mixed crystals changes with the temperature, the percentage of potassium nitrate being 20 and 50 per cent. at 182° , 20 and

69 per cent. at 133°, and 35 and 84 per cent. at 108·5°. This system thus forms a complete example of the type 4 of transition curve deduced by Roozeboom (preceding abstracts). L. M. J.

Cryoscopic Researches on the Constitution of Acid Amides. By KARL AUWERS [with MAX DOHRN] (*Zeit. physikal. Chem.*, 1899, 30, 529—544).—It has been shown that amides in naphthalene solution are generally cryoscopically abnormal (compare Abstr., 1897, ii, 476). The constitution may be either $R \cdot NH \cdot CO \cdot R'$ or $RN : CR' \cdot OH$, and in the latter case the abnormality may be occasioned by the hydroxyl group and the behaviour of the thioamides should be similar to that of the thiophenols. The thiophenols examined, however, were found to be cryoscopically normal, and the thioamides to be abnormal, so that the constitution $R \cdot NH \cdot CS \cdot R'$ is most probable. As, however, the abnormality may be due to the increased acidity of the thio-compounds, the case was further examined. The author shows that in general a substituent causes a decrease of abnormality only when this substituent and the group causing abnormality are attached to neighbouring carbon atoms. In the case of substituted derivatives of benzanilide, it was found that the compounds from ortho-substituted aniline are normal, but the derivatives of the ortho-substituted benzoic acid remain abnormal, and hence the abnormality is caused by an $\cdot NH$ group, that is, the previous conclusions are confirmed. Basic amines are, however, normal, although piperidine is slightly abnormal, and it is found that the abnormality of urethane is greatly decreased by the entrance of a phenyl group. L. M. J.

Accurate Determination of the Molecular Weight of Gases from their Density. By JOHANNES D. VAN DER WAALS (*Proc. K. Akad. Wetensch. Amsterdam*, 1898, 1, 198—201).—The molecular weight of a gas is proportional to the normal density d_n , which is equal to $d_0/(1+a)(1-b)$, where d_0 is the density found at 0° under the pressure p_0 , and a and b are the constants of van der Waals' equation. If d'_0 be the density found at another temperature T , mathematical discussion leads to the equation $d_n/d'_0 = 1 - 0\cdot001645T_k/T(27T_k/8T - 1)$, where T_k is the critical temperature of the gas. For $T > 27T_k/8$, the correction is negative, and d_n/d'_0 has a maximum for $T = 27T_k/4$.

The condition for the observation under a pressure of $11/76$, without the vapour being saturated, is that T must not fall below a certain limit. When this limit is put at $T_k/1\cdot6$, the normal density is 1 per cent. smaller than the value given by experiment. J. C. P.

True Density of Chemical Compound and its Relation to Composition and Constitution. By INNOCENTIUS I. KANONNIKOFF (*Chem. Centr.*, 1899, ii, 858—861; from *J. Russ. Chem. Soc.*, 31, 573—640).—According to the theories of Clausius and Mosotti, the ratio $\mu^2 - 1/\mu^2 + 2$, where μ is the refractive index, is the ratio of the actual volume of the molecules to the total volume; the true density is hence $d(\mu^2 + 2/\mu^2 - 1) = D$, and the value of this constant is the same for liquid and gaseous states. The value being, however, dependent on that of the refractive index, is obviously a function of wave-length and temperature, and may, if required, be corrected for

an infinite wave-length and for zero temperature by the Cauchy dispersion formula and the expression $D^t = D_0(1 + kt)$. The author, however, employs the values for sodium light and a temperature of from 10° to 20° . If the true density is multiplied by the molecular weight, the product, termed the "molecular density," but of which the physical interpretation does not appear evident, is found to be an additive function. In hydrocarbons, it is given by the expression $39.7n + (2n \pm m)H - 4H + a.9H - b.6H - b'.26H - c.4H$, where n is the number of carbon atoms, $2n \pm m$ that of the hydrogen atoms, and a , b , b' , and c the number of closed chains, ethylenic unions, naphthaleno-ethylenic unions, and acetylenic unions respectively in the molecule, the value for H being 0.967. It is stated that for a large number of compounds the values so calculated are in accord with the determinations. In many cases, the "molecular density" may be a useful criterion of constitution, as the various modes of union have very diverse values, and various examples are given. L. M. J.

Equation of Condition. By MAX REINGANUM (*Chem. Centr.*, 1889, ii, 955; from *Diss. Göttingen*).—Van der Waals' equation can be regarded only as an approximation, but any improvement suggested must still necessitate the law of corresponding states. The author suggests the equation $\{p + a/v^2\}/\{(v - b)^4/v^3\} = RT$; this contains no more constants than van der Waals' expression; the constants also are functions of the molecular weight, and apparent and actual molecular volumes. The author states that it gives results in good accord with previous determinations, notably, those of Young on isopentane, and the validity of the equation is proved by the coincidence of the isothermals, and by the comparison of the predicted and found vapour pressure, expansion of liquid and vapour, and latent heat of vaporisation. The equation predicts the constant ratio between the critical and actual molecular volumes and the constant ratio of the critical density to the theoretical density calculated for a perfect gas, whilst the deduced temperature coefficients of internal friction are also in agreement with the experimental results.

L. M. J.

Equilibrium in the System, Water—Phenol—Aniline. By FRANS A. H. SCHREINEMAKERS (*Zeit. physikal. Chem.*, 4899, 30, 460—480).—The theoretical aspects of such an equilibrium system are fully considered; in it, two pairs of the components are capable of forming two liquid layers as in the system, water—alcohol—succinonitrile (*Abstr.*, 1898, ii, 564), but the case is now complicated by the existence of a compound of phenol and aniline. In such a case, by the addition of water to the compound, two liquid phases may result in which (1), with or without decomposition, the relative concentrations of the two components of the compound are unchanged, or (2) owing to decomposition, the relative concentrations vary. In the first case, only one temperature occurs at which the compound and the two liquid phases can exist together, but in the second a series of temperatures occur, that is, a "transition interval." This interesting case is observed in the system considered, the compound of phenol and aniline being in equilibrium with two liquid phases between the temperatures

16.9° and 17.2°. The various theoretical and determined equilibrium curves and isothermals are given in the paper (Abstr., 1899, ii, 739).
L. M. J.

False Equilibrium. By MAX BODENSTEIN (*Zeit. physikal. Chem.*, 1899, 30, 567—569).—A reply to Duhem's criticisms of the author's results (see Abstr., 1899, ii, 739).
L. M. J.

Condition of Substances Insoluble in Water formed in Gelatin. By CORNELIS A. LOBRY DE BRUYN (*Proc. K. Akad. Wetensch. Amsterdam*, 1898, 1, 39—42).—The exceptional phenomenon of certain substances, such as silicic acid, remaining unprecipitated in aqueous solution, is general in aqueous gelatin solution. An insoluble compound formed by double decomposition in aqueous solution generally remains unprecipitated when the same substances are brought together in gelatin solution, although there are grounds for believing that the double decomposition has actually taken place. Thus, Cohen has shown that when silver nitrate and potassium bromide are mixed in gelatin solution, the resulting conductivity is that due to the potassium nitrate, and not that due to the two electrolytes, silver nitrate and potassium bromide. Further, although the gelatin solution remains transparent, it takes the colour of the product formed by double decomposition, as in the cases of Prussian blue and lead iodide.

Although the visible precipitation of amorphous substances is prevented by gelatin, crystalline, insoluble substances separate as in aqueous solution: this is the case, for example, with calcium oxalate and ammonium magnesium phosphate.
J. C. P.

Genesis of Dalton's Atomic Theory. By HEINRICH DEBUS (*Zeit. physikal. Chem.*, 1899, 30, 556—562).—A further controversial paper in reply to Kahlbaum (Abstr., 1899, ii, 740).
L. M. J.

Some Anomalies in Mendeléeff's System. By THEODOR H. BEHRENS (*Proc. K. Akad. Wetensch. Amsterdam*, 1898, 1, 148—151).—Isomorphism is not to be rashly used as a guide to the natural position of an element, for the evidence is often conflicting. Retgers, who denies isomorphism between tellurates and sulphates, assigns to tellurium a place in the eighth group between ruthenium and osmium, disregarding the analogy between hydrogen telluride and sulphide, and recognising the isomorphism of K_2TeCl_6 with K_2OsCl_6 and K_2IrCl_6 . But, on other grounds, tellurium might be put in the fourth group, for the compounds Cs_2TeCl_6 and Cs_2SnCl_6 are isomorphous, and tellurium dioxide dissolves in potassium hydrogen oxalate, forming crystals like those of potassium zirconium oxalate; further, if tellurium should be placed between ruthenium and osmium, seventeen new elements would have to be looked for in that group.

With manganese, there is a similar ambiguity. The isomorphism between $KMnO_4$ and $KClO_4$ agrees with the position of manganese in the seventh group, but, on the other hand, K_2MnO_4 and K_2SO_4 are isomorphous, and experiments made with manganese tetrachloride point to an analogy between manganese and tin.
J. C. P.

Relation of Physical Properties of Elements to their Atomic Weights. By W. SANDER (*Chem. Centr.*, 1899, ii, 955 ; from *Electr. Zeit.*, 6, 133).—Curves are given in the original paper from which the author deduces that the coefficients of linear expansion, migration velocities of ions, electrical conductivity, and electrolytic potential of metals are periodic functions of their atomic weights.

L. M. J.

Inorganic Chemistry.

Nitrosyl Chloride and its Compounds. By W. J. VAN HETEREN (*Zeit. anorg. Chem.*, 1899, 22, 277—278).—Nitrosyl chloride, when cooled in a mixture of solid carbon dioxide and alcohol, solidifies in blood-red crystals which melt at -65° . It mixes in all proportions with liquid chlorine, and a mixture in the proportions required by the formula NOCl_3 does not crystallise at -80° . The compound, $\text{SnCl}_4 \cdot 2\text{NOCl}$, prepared by treating stannic chloride with nitrosyl chloride and distilling off the excess, melts in a sealed tube at 150° . The compound $2\text{SbCl}_5 \cdot 5\text{NOCl}$ melts in a sealed tube at 180° , and the compound $\text{Fe}_2\text{Cl}_6 \cdot 2\text{NOCl}$ at 116° .
E. C. R.

The Lower Oxides of Phosphorus. By AUGUST MICHAELIS and M. PITTSCH (*Annalen*, 1899, 310, 45—74. Compare Abstr., 1899, ii, 285).—Phosphorus suboxide, P_4O , first obtained by Le Verrier, is precipitated on adding an acid to a solution of phosphorus in alcoholic potash diluted with water; it is also formed on withdrawing the elements of water from hypophosphorous acid by the action of acetic anhydride. It is an orange-red powder of sp. gr. 1.9123 at 26° , but the colour depends largely upon the state of division, being sometimes pale yellow. When thoroughly dried, it is almost odourless, but a trace of moisture imparts to it the odour of phosphine; in the former condition, also, it may be heated in air to a comparatively high temperature without becoming ignited, but when moist it burns readily after being heated at 90° during several hours. If dried and heated in an indifferent gas, phosphorus distils over, leaving phosphoric oxide. Chlorine converts the dried oxide into phosphorus oxychloride and phosphorus pentachloride, the damp substance being oxidised to phosphoric acid, which is also produced by the action of sodium hypochlorite and of warmed sulphuric acid, the latter becoming reduced to hydrogen sulphide. Concentrated nitric acid ignites the substance, which is indifferent towards hydrochloric acid. Many metals are precipitated by it from solutions of their salts either in metallic form, or as phosphorus compounds. A solution of sodium or potassium hydroxide in aqueous alcohol dissolves phosphorus suboxide, forming a deep red solution which transmits only light between the C and D lines of the spectrum; when warmed, or on standing at the ordinary temperature, this solution evolves hydrogen and phosphine, sodium hypophosphite

remaining dissolved. The oxide is coloured brown by ammonia, but the latter is removed on exposure to air, and the substance regains its orange-red hue.

The result of the authors' investigation is to show that phosphorus suboxide is the only lower oxide of phosphorus existing at present, those of Gautier, Besson, and Franke being merely Le Verrier's compound in an unpurified condition. An examination of these supposed oxides has been made, and is described in the paper, which gives details of the analytical methods employed [compare Chapman and Liddbury, *Trans.*, 1899, 75, 973]. M. O. F.

A General Property of Phosphorous Acid. By LUDWIG VANINO (*Chem. Centr.*, 1899, ii, 930; from *Pharm. Centr.-H.*, 40, 637—668).—When sodium hydroxide solution is added to a mixture of 10 grams of a 10 per cent. solution of copper sulphate with several grams of phosphorous acid, only a faint turbidity is produced, and this disappears on further addition of the alkali. Under similar conditions, salts of the alkaline earths, cobalt, nickel, and iron (ferrous or ferric) also form clear, alkaline solutions. This property, however, is limited to those metals which form hydroxides, precipitates being formed in the case of salts of such metals as silver or mercury (mercurous or mercuric). These alkaline solutions do not usually form precipitates with sodium carbonate, but often give remarkable reactions with hydrogen sulphide or ammonium sulphide. The alkaline solution of a manganese salt is not at first attacked by hydrogen sulphide, and a similar solution of a ferric salt also resists the action of ammonium sulphide. The copper sulphate solution is not acted on by sodium carbonate or ammonium thiocyanate, but is reduced by a trace of dextrose. Although satisfactory results have not been obtained by analysis, it is probable that in this case, as in the case of arsenious acid, salts such as CuHPO_3 are formed, and that these then combine with sodium phosphate to form double salts. E. W. W.

Fluorohyperborates. By PETR G. MELIKOFF and S. LORD-KIPANIDZE (*Ber.*, 1899, 32, 3349—3354. Compare *Abstr.*, 1898, ii, 219 and 292).—*Potassium fluorohyperborate*, $\text{K}_4\text{B}_4\text{F}_{11}\text{O}_{11} + \text{H}_2\text{O}$, produced by treating an aqueous solution of potassium fluoroborate, $2\text{KF}\cdot\text{B}_2\text{O}_3$, with a slightly alkaline solution of hydrogen peroxide, separates on the addition of alcohol as a viscous mass which becomes crystalline on stirring; the substance is redissolved in water and the process repeated, the salt being finally obtained in rhombic prisms. The following constitution, $\text{OK}\cdot\text{BF}\cdot\text{O}\cdot\text{O}\cdot\text{BF}\cdot\text{O}\cdot\text{OK}, \text{OK}\cdot\text{O}\cdot\text{BF}\cdot\text{O}\cdot\text{O}\cdot\text{BF}\cdot\text{O}\cdot\text{OK}, \text{H}_2\text{O}$, is assigned to the compound. The aqueous solution has an alkaline reaction and slowly evolves oxygen at the ordinary temperature, this decomposition being accelerated by warming; the silver salt is produced as a yellow precipitate by adding silver nitrate to the solution; it is unstable, and blackens owing to the separation of metallic silver, oxygen being simultaneously evolved. The dry potassium salt is moderately stable; dilute sulphuric acid liberates hydrogen peroxide, whilst the concentrated acid evolves ozonised oxygen. This salt may also be obtained by the action of hydrogen peroxide on potassium orthofluoroborate, $\text{BF}(\text{OK})_2$. G. T. M.

Fluorohyperborates. By PETR G. MELIKOFF and S. LORD-KIPANIDZE (*Ber.*, 1899, 32, 3510—3512. Compare preceding abstract).

—The *potassium* salt, $K_2B_2F_2O_6 + H_2O$, to which the structure

$$O_2(BF \cdot O \cdot OK)_2 + H_2O$$

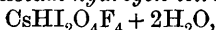
is assigned, is precipitated by alcohol from hydrogen peroxide solution as a crystalline powder. The *ammonium* salt, $Am_2B_2F_2O_6 + 3H_2O$, prepared by adding hydrogen peroxide, ammonia, and alcohol to a solution of boric acid and ammonium fluoride, is a white, crystalline powder, and is moderately stable; the aqueous solution decomposes gradually at ordinary temperatures, and rapidly on warming.

T. M. L.

Explosion of Potassium Chlorate. By MARCELLIN P. E. BERTHELOT (*Compt. rend.*, 1899, 129, 926—929).—Although the decomposition of potassium chlorate into the chloride and oxygen is an exothermic reaction, it is not regarded as an explosive, since it does not detonate when gradually heated. If, however, the melted chlorate be allowed to fall drop by drop into a glass tube heated to redness, a sharp and rather prolonged explosion occurs as each drop comes into contact with the hot tube, a white smoke of potassium chloride being simultaneously formed.

T. H. P.

Acid Iodates Containing Fluorine, and Cæsium Fluoroperiodate. By RUDOLPH F. WEINLAND and O. KÖPPEN (*Zeit. anorg. Chem.*, 1899, 22, 256—265).—*Cæsium hydrogen tetrafluoriodate*,



is obtained by dissolving cæsium hydrogen iodate, cæsium dihydrogen iodate, or cæsium dihydrogen iodate with 2 mols. iodic acid in 20—60 per cent. hydrofluoric acid, and also in smaller quantities from a solution of cæsium iodate in hydrofluoric acid. It crystallises from 40—60 per cent. hydrofluoric acid in thick, six-sided plates, or aggregates of thin plates, effloresces rapidly on exposure to the air, and dissolves slowly in water, yielding a strongly hydrofluoric acid solution.

Rubidium hydrogen tetrafluoriodate, with $2H_2O$, is obtained by dissolving rubidium fluoride (1 mol.) and iodic acid (2 mols.) in hydrofluoric acid of at least 40 per cent. It crystallises in plates, and is very easily converted into rubidium difluoriodate.

Cæsium fluoroperiodate, $2CsIO_4 \cdot 3HF + H_2O$, obtained by dissolving cæsium periodate in warm 60 per cent. hydrofluoric acid, crystallises in colourless, lustrous prisms, effloresces slowly on exposure to the air, and is decomposed by water.

E. C. R.

Reversible Reaction between Hydrogen Chloride and Silver. By JOUNIAUX (*Compt. rend.*, 1899, 129, 883—886. Compare Abstr., 1879, 589).—The amount of hydrogen chloride formed when silver chloride and hydrogen are heated together increases with the time of heating, and reaches a limit which is dependent on the temperature to which the reacting substances are heated. At a temperature of 350° , equilibrium is established when the residual gas contains 75.85 per cent. of hydrogen chloride, and is attained after heating for 5 weeks, whilst at 600° the limit is reached after heating for 1 hour, and the residual gas contains 92.80 per cent. of hydrogen chloride. The action of hydrogen chloride on silver is also limited and

varies with the temperature. At 490° , 530° , and 600° , equilibrium is established when the residual gas contains 94.10, 92.95, and 92.80 per cent. of hydrogen chloride respectively. The limit at which equilibrium is established is practically independent of the amount of surface of silver chloride exposed, and for temperatures above the melting point of silver chloride this limit is quite independent of mass.

H. R. LE S.

Reciprocal Displacement of Metals. By ALBERT COLSON (*Compt. rend.*, 1899, 129, 825—827).—Experiments with silver and mercurous chloride, and silver and mercuric sulphide in sealed vacuous tubes between 150° and 300° , show that the direct displacement of silver by mercury is, under some conditions, a reversible reaction, limited by the pressure of the mercury vapour, just as heterogeneous dissociation is limited by a gaseous pressure.

Experiments with copper and cadmium sulphide or oxide gave similar, but less definite, results owing to the partial direct dissociation of the two cadmium compounds below 600° . Thin films of cadmium formed by condensation of the vapour in the cool parts of the tube were violet-blue by transmitted light.

C. H. B.

Preparation of Monocalcium Phosphate. By L. LÉON A. PRUNIER and ADOLPHE JOUVE (*J. Pharm.*, 1899, [vi], 10, 529—530).—If a mixture of dicalcium phosphate, $\text{Ca}_2\text{H}_2(\text{PO}_4)_2$, and orthophosphoric acid in the proportions to form monocalcium phosphate, $\text{CaH}_4(\text{PO}_4)_2$, is dissolved in an equal weight of water and the solution rapidly evaporated, a deposit of dicalcium phosphate, sometimes mixed with a little of the monocalcium salt, is obtained; whereas, if the liquid is subjected to prolonged boiling, only hydrated monocalcium phosphate is formed. From these results, it is concluded that the formation of the more stable hydrated monocalcium phosphate from the anhydrous salt is only slowly effected, and this is confirmed by the fact that the pure anhydrous salt only is precipitated when alcohol is added to the freshly prepared solution.

N. L.

Change of Volume during the Hardening of Hydraulic Cements. By HENRI LE CHATELIER (*Compt. rend.*, 1899, 129, 1232—1234).—The author's experiments indicate that the apparent expansion of mortars and cements during hydration is due to the relative displacement of the solid particles, and that in reality this action is accompanied by a considerable diminution in volume.

G. T. M.

Action of Hydrogen Fluoride and Fluorine on Glass. By HENRI MOISSAN (*Compt. rend.*, 1899, 129, 799—804).—Hydrogen fluoride, produced by heating carefully dried potassium hydrogen fluoride, acts at once on very carefully dried glass at the ordinary temperature. Gaseous fluorine obtained by electrolysis, and deprived as far as possible of hydrogen fluoride by passing it over sodium fluoride, acts on glass, but if hydrogen fluoride is completely removed by subjecting the fluorine to the temperature of boiling air, or by passing the gas over dry sodium fluoride cooled in a mixture of solid carbon dioxide and acetone, the fluorine no longer acts on glass, even at 100° , provided that it is dry and the surface is free from

organic matter. If these conditions are satisfied, liquid fluorine can be kept for a long time in sealed glass bulbs or tubes.

The author points out that glass may retain its polish even when acted on by hydrogen fluoride, and that phosphoric oxide cannot be used for drying hydrogen fluoride, owing to the formation of phosphorus oxyfluoride at the ordinary temperature. C. H. B.

Activity of Manganese in Promoting the Phosphorescence of Strontium Sulphide. By JOSÉ R. MOURELO (*Compt. rend.*, 1899, 129, 1236—1238. Compare Abstr., 1899, ii, 97, 98, 366, 420, and 484).—The paper contains details of the preparation of phosphorescent strontium sulphide produced by the action of sulphur on strontium carbonate or sulphate at a red heat in the presence of small quantities of manganous sulphate, sodium chloride and sodium carbonate. The effect of the manganous sulphate on the strontium sulphide is similar to that of manganous carbonate or basic bismuth nitrate; the phosphorescence becomes more intense, lasts longer, and is attained after a shorter exposure to diffused daylight. When due to manganese, the phosphorescence has a yellowish-green colour, whilst that produced by bismuth is bluish-green. G. T. M.

Effect of various Solvents on the Allotropic Change of Mercuric Iodide. By J. H. KASTLE and MARY E. CLARK (*Amer. Chem. J.*, 1899, 22, 473—484).—The authors have studied the behaviour of mercuric iodide when dissolved in the following liquids at their boiling point: ethyl bromide, propyl chloride, acetone, ethylidene chloride, ethyl iodide, ethyl acetate, alcohol, isopropyl bromide, benzene, allyl alcohol, toluene, propionitrile, ethyl butyrate, isobutyrate and propionate, benzoic acid, phenol, benzonitrile, oil of winter green, propyl bromide, *ψ*-cumene, naphthalene and phenyl salicylate; with all these solvents, except isobutyl bromide and propyl chloride, yellow solutions were obtained, and in all cases, without exception, yellow crystals separated on cooling; the pink colour of the solutions obtained with isobutyl bromide and propyl chloride appears to be due, not to the red modification of mercuric iodide, but "to the formation of unstable alkyl iodides." The fact that only yellow solutions are obtained on dissolving the red iodide in the various solvents and that the yellow modification alone separates from these, appears to indicate that the transition temperature (128°) of mercuric iodide is lowered by the solvents dealt with, especially by those boiling at a low temperature. The question whether red mercuric iodide is insoluble in the solvents named, and only dissolves by being converted into the yellow modification, is discussed at some length. It is significant that the red modification is not obtained, but only crystals of the yellow variety, on adding a red crystal to the yellow solutions. W. A. D.

Transformation Temperature of the Quadratic and Orthorhombic Forms of Mercuric Iodide. By DESIRÉ GERNEZ (*Compt. rend.*, 1899, 129, 1234—1236).—Yellow mercuric iodide may be kept for a long time at the ordinary temperature, whilst the red variety persists at temperatures above that at which transformation is possible; the former state of the iodide is termed "crystalline superfusion,"

and the latter "crystalline superheating." On account of these retardations, it is difficult to determine the transformation temperature with exactness. When alternate layers of the two forms, placed in contact with each other, are maintained at the same temperature, it is found that at 127° the zones of yellow iodide slowly encroach on the red variety, whilst at 125° this modification gradually displaces the other. The transformation temperature is therefore 126° and is the same whether the crystals are heated under atmospheric pressure or in a vacuum.

G. T. M

Dissociation by Water of Ammonium and Potassium Mercuriodides. By MAURICE FRANÇOIS (*Compt. rend.*, 1899, 129, 959—962. Compare Abstr., 1899, ii, 597).—In the presence of relatively large quantities of water, these salts suffer complete decomposition into the constituent iodides, part of the mercuric iodide being precipitated and the rest forming a saturated solution in the alkali iodide solution. By treatment of the mercuriodides with small quantities of water, as also by acting on excess of mercuric iodide with solutions of the alkali iodides, it is found that the decomposition is limited and reversible, and obeys the laws of dissociation of salts by water; when equilibrium is attained, the liquid contains a quantity of free ammonium or potassium iodide, which is constant for a given temperature.

T. H. P.

Preparation of Sulphur, Chlorine, and Bromine Compounds of the Cerite Metals. By WILHELM MUTHMANN and L. STÜTZEL (*Ber.*, 1899, 32, 3413—3419).—Didier's method of preparing cerium and lanthanum sulphides, by passing hydrogen sulphide over the heated oxides (Abstr., 1885, 955), does not give satisfactory results unless the oxide is very finely powdered; the pure sulphides can, however, be readily obtained if the anhydrous sulphates are used. The cerium sulphide is brownish-black to black, lanthanum sulphide is pure yellow, neodymium sulphide is olive-green, and praseodymium sulphide is chocolate-coloured. They are fairly stable in air at the ordinary temperature, but are slowly decomposed by boiling water with evolution of hydrogen sulphide (lanthanum sulphide the most readily), and dissolve readily in dilute acids; the four sulphides ignite readily below a red-heat and burn to a mixture of oxide and sulphate, and cerium sulphide when finely divided ignites spontaneously at the ordinary temperature. Mosander's greenish cerium oxysulphide and golden-yellow, crystalline sulphide could not be prepared. The densities are La_2S_3 , 4.9108; Ce_2S_3 , 5.020; Pr_2S_3 , 5.042; Nd_2S_3 , 5.179 at 11° , increasing with the atomic weight.

The chlorides are prepared by first passing hydrogen sulphide over the dry sulphates, then carbon dioxide and dry hydrogen chloride. Cerium and lanthanum chlorides are pure white, crystalline masses, neodymium chloride is rose-coloured, and praseodymium is green. They readily absorb moisture from the air, dissolve with hissing in water to a clear solution, dissolve in alcohol and are readily fusible, but only volatilise with great difficulty. For preparing large quantities of chloride containing a trace of oxide, the best method is by evaporation and ignition of the ammonium double chloride.

By passing hydrogen bromide over the sulphide, cerium bromide, CeBr_3 , was obtained as a snow-white, crystalline, soluble powder, which readily absorbed moisture from the air. T. M. L.

Specific Gravity of Yttrium, Zirconium, and Erbium. By STEFAN MEYER (*Monatsh.*, 1899, 20, 793—796).—Investigations of magnetic susceptibility have shown that the paramagnetic element yttrium occupies a position in the periodic system among a number of diamagnetic elements, and this peculiarity has led the author to determine some other characteristic constant. The specific gravity of yttrium powder was measured in a volumenometer, the powder being contained in a small tube connected through a ground stopper with the rest of the apparatus. The specific gravity was found to be 3.80 at 15°; with the atomic weight 89, the atomic volume is thus 23.6, a value corresponding with the position already assigned to yttrium in the periodic system. The abnormal magnetic behaviour of this element is therefore probably due to an admixture of some known or unknown element; if the presence of the new element victorium in yttrium should be confirmed, the former must be strongly paramagnetic.

The specific gravity of zirconium has been found to be 4.08, and that of erbium 4.77 at 15°. J. C. P.

Direct Combination of Aluminium and Nitrogen in the Electric Arc. By LEO ARONS (*Chem. Centr.*, 1899, ii, 643; from *Naturw. Rundsch.*, 14, 453—454).—When an electric arc is produced between electrodes of platinum, zinc, copper, tin, lead, iron, or cobalt in an atmosphere of nitrogen, the surface of the metal becomes coated with a film which probably consists of nitride. In the case of aluminium, considerable quantities of the greyish-black nitride are formed. This nitride is insoluble in water, and when treated with potassium hydroxide solution yields ammonia. When silver electrodes are used, the appearance of the silver changes, but there is apparently no formation of nitride. The analogy between the production of nitrides and that of acetylene by means of the arc, and the importance of utilising the nitrogen of the atmosphere are pointed out.

E. W. W.

Double Salts of Ferric and Aluminium Fluorides with Fluorides of Bivalent Metals. By RUDOLPH F. WEINLAND and O. KÖPPEN (*Zeit. anorg. Chem.*, 1899, 22, 266—276).—These salts are prepared by mixing a solution of aluminium or ferric hydroxide in dilute hydrofluoric acid with a solution of the carbonate or hydroxide of the bivalent metal in dilute hydrofluoric acid, and allowing the mixture to evaporate at the ordinary temperature over lime. An excess of one of the constituents and the amount of hydrofluoric acid present are immaterial. The salts can be recrystallised from dilute hydrofluoric acid.

Ferric ferrous fluoride, $\text{FeF}_3 \cdot \text{FeF}_2 + 7\text{H}_2\text{O}$, forms yellow, rhomboidal crystals and does not effloresce over sulphuric acid. *Ferric nickel fluoride*, $\text{FeF}_3 \cdot \text{NiF}_2 + 7\text{H}_2\text{O}$, separates in small, bright green crystals, *ferric cobalt fluoride* in rose-coloured crystals, and *ferric zinc fluoride* in very small, faintly red crystals.

Aluminium ferrous fluoride, $\text{AlF}_3 \cdot \text{FeF}_2 + 7\text{H}_2\text{O}$, forms small, greenish-white, rhomboidal crystals, does not oxidise on exposure to the air or effloresce when placed over sulphuric acid. The corresponding *nickel* salt separates in green crystals, the *cobalt* salt in reddish-white crystals, and the *zinc* salt in colourless crystals.

Aluminium fluoride combines with copper fluoride to form three double salts. The salt, $\text{AlF}_3 \cdot 2\text{CuF}_2 + 11\text{H}_2\text{O}$, obtained from solutions containing 1 mol. aluminium fluoride to 2 or more mols. copper fluoride, crystallises in spherical aggregates of blue leaflets and does not effloresce over sulphuric acid. The salt, $2\text{AlF}_3 \cdot 3\text{CuF}_2 + 18\text{H}_2\text{O}$, crystallises in deep blue prisms resembling feldspar from solutions containing 2 mols. aluminium fluoride to 3 mols. copper fluoride in the presence of only small quantities of hydrofluoric acid. If much acid is present, the salt, $\text{AlF}_3 \cdot \text{CuF}_2 \cdot \text{HF} + 8\text{H}_2\text{O}$, is formed; this crystallises in large, blue rhombohedra from solutions containing 1 mol. aluminium fluoride to 1 mol. or less of copper fluoride and an excess of hydrofluoric acid, and effloresces rapidly on exposure to the air with evolution of water and hydrofluoric acid.

E. C. R.

Action of Nitric Oxide on Chromyl Dichloride. By VICTOR THOMAS (*Compt. rend.*, 1899, 129, 828—831).—Nitric oxide acts violently on chromyl dichloride with abundant formation of higher nitrogen oxides. If the chromium compound is in the form of vapour, the solid product is at first white, but afterwards becomes brown; it is very slightly soluble in organic solvents, but dissolves readily in water with liberation of nitrogen oxides and production of a black solution containing chromic oxide, chromic acid, chlorine, and nitrogen oxides. This solid product has the composition $\text{Cr}_5\text{Cl}_5\text{O}_7 \cdot 2\text{NO}_2$; when heated, it yields chromic oxide, nitrogen oxides, and chlorine, and when treated with reducing agents the nitrogen is converted into ammonia. Chromium, like tin, bismuth, and iron, can evidently form compounds containing the NO_2 group, which are stable even in a vacuum at the ordinary temperature, but are readily decomposed by water.

C. H. B.

Molybdenum Disulphide. By MARCEL GUICHARD (*Compt. rend.*, 1899, 129, 1239—1242).—Crystalline molybdenum disulphide is readily prepared by heating a mixture of potassium carbonate, sulphur, and molybdenum dioxide or ammonium molybdate in the Perrot furnace. The amorphous sulphide is produced by heating a mixture of ammonium molybdate and sulphur in an earthenware crucible surrounded by lampblack, the operation being repeated to remove the last traces of oxygen from the product. The sulphide is not attacked by solutions of sulphur in alkaline hydrosulphides or sulphur chloride, and phosphorus is without action on it even at high temperatures. When heated in a current of hydrogen, it is directly reduced to the metal without forming a lower sulphide. Although native molybdenite loses the whole of its sulphur at the temperature of the electric arc, it is possible in the case of the artificial product to isolate an intermediate sesquisulphide.

G. T. M.

Molybdenum Silicide. By ÉMILE VIGOUROUX (*Compt. rend.*, 1899, 129, 1238—1239).—*Molybdenum silicide*, Mo_2Si_3 , resembles tungsten

silicide (Abstr., 1899, ii, 194), and is prepared in a similar manner by heating, in a carbon crucible in the electric furnace, a mixture of crystallised silicon and the molybdenum oxides obtained by calcining ammonium molybdate; the crystalline product is disintegrated by electrolysis in hydrochloric acid, and the mixture of crystalline silicides is treated successively with aqua regia, caustic potash, and hydrofluoric acid; the removal of carbon silicide is effected by means of cadmium tungstate solution, and the residue consists of molybdenum silicide mixed with more or less iron silicide. When heated in chlorine at 300° , molybdenum silicide becomes ignited, silicon tetrachloride and molybdenum perchloride being produced. G. T. M.

Complex Inorganic Acids. VIII. Arsenoduodecitungstic Acid and Arsenoluteotungstic Acid. By FRIEDRICH KEHRMANN and E. RÜTTIMANN (*Zeit. anorg. Chem.*, 1899, 285—296).—*Ammonium arsenoduodecitungstate*, $3(\text{NH}_4)_2\text{O}, \text{As}_2\text{O}_5, 24\text{WO}_3 + 12\text{H}_2\text{O}$, obtained by adding arsenic acid to a concentrated aqueous solution of sodium tungstate, then adding hydrochloric acid in excess and ammonium chloride, and heating to boiling, is a snow-white, crystalline powder resembling the analogous phosphorus compound. A solution of the acid is obtained by dissolving the salt in aqua regia, but decomposes on evaporation. When boiled with a 5 per cent. solution of ammonium carbonate, it is converted into the 22-acid and on adding barium chloride to the solution the *barium salt*, $7\text{BaO}, \text{As}_2\text{O}_5, 22\text{WO}_3$, separates in small, lustrous octahedra.

Ammonium arsenoluteotungstate, $3(\text{NH}_4)_2\text{O}, \text{As}_2\text{O}_5, 18\text{WO}_3 + 14\text{H}_2\text{O}$, obtained by heating sodium tungstate with a syrupy solution of arsenic acid and precipitating with solid ammonium chloride, crystallises in monoclinic, lemon-yellow prisms and is very soluble in cold water. When treated with ammonium carbonate, it is converted into the *salt* $5(\text{NH}_4)_2\text{O}, \text{As}_2\text{O}_5, 17\text{WO}_3 + 8\text{H}_2\text{O}$, which crystallises in thick, white, semi-transparent crystals, and is decomposed by boiling with water with evolution of ammonia.

Potassium arsenoluteotungstate, when treated with potassium hydrogen carbonate, yields the *salt* $5\text{K}_2\text{O}, \text{As}_2\text{O}_5, 17\text{WO}_3 + 22\text{H}_2\text{O}$, which crystallises in lustrous, white leaflets, and is not decomposed by boiling with water. E. C. R.

Antimonic Acid and Antimonates. By A. E. DELACROIX (*Bull. Soc. Chim.*, 1899, [iii], 21, 1049—1054. Compare Abstr., 1898, ii, 340).—The two soluble antimonic acids, the existence of which in solution has previously been demonstrated, are more suitably termed tetra-antimonic and triantimonic acids instead of pyroantimonic and orthoantimonic acids respectively.

Tetra-antimonic acid is obtained, by freezing its aqueous solution, in the form of thin, optically active scales having the composition $\text{Sb}_2\text{O}_5, 4\text{H}_2\text{O}$, or, when dried over sulphuric acid, $\text{Sb}_2\text{O}_5, 3\text{H}_2\text{O}$; a further H_2O is lost at 100° . It forms both monobasic and dibasic salts of the composition $\text{M}_2\text{O}, 4\text{Sb}_2\text{O}_5$ and $\text{M}_2\text{O}, 2\text{Sb}_2\text{O}_5$ respectively. The alkali salts are soluble in water, but not in solutions of other salts, and are prepared by adding to a solution of the acid the theoretical amount of alkali hydroxide or acetate, and freezing the liquid, when

the salts are obtained in the crystalline form; the dibasic alkali salts are precipitated in an amorphous state by adding alcohol to their solutions. The other tetra-antimonates are obtained by double decomposition from the metallic acetates, and are insoluble in water. The following salts have been prepared; some of them, the dibasic sodium salt, for instance, are decomposed by water, with the production of monobasic and dibasic triantimonates. $\text{Na}_2\text{O}, 2\text{Sb}_2\text{O}_5 + 9\text{H}_2\text{O}$; $\text{Na}_2\text{O}, 4\text{Sb}_2\text{O}_5$; the mixed salt, $\text{Na}_2\text{O}, 4\text{Sb}_2\text{O}_5, \text{Na}_2\text{O}, 2\text{Sb}_2\text{O}_5 + 20\text{H}_2\text{O}$; $\text{K}_2\text{O}, 2\text{Sb}_2\text{O}_5 + 9\text{H}_2\text{O}$; $\text{BaO}, 2\text{Sb}_2\text{O}_5 + 5\text{H}_2\text{O}$; $\text{BaO}, 4\text{Sb}_2\text{O}_5 + 15\text{H}_2\text{O}$; $\text{CuO}, 2\text{Sb}_2\text{O}_5 + 9\text{H}_2\text{O}$, a green salt which dissolves in ammonia to form a double salt crystallising in hexagonal prisms. Tetra-antimonates of silver, cadmium, mercury, nickel, and cobalt have also been obtained; the nickel and cobalt salts form respectively red and blue double salts with ammonia.

Triantimonic acid is obtained, by freezing its solution, in crystals of the composition $\text{Sb}_2\text{O}_5, 3\text{H}_2\text{O}$, which lose $1\text{H}_2\text{O}$ when dried over sulphuric acid. It forms salts of the types $\text{M}_2\text{O}, 3\text{Sb}_2\text{O}_5$, $2\text{M}_2\text{O}, 3\text{Sb}_2\text{O}_5$, and $3\text{M}_2\text{O}, 3\text{Sb}_2\text{O}_5$, besides other more complex derivatives, which are prepared by methods similar to those employed in the preparation of tetra-antimonates. The alkali salts only are soluble in water, those containing one equivalent of the base being also soluble in alcohol. The following triantimonates have been obtained: $2\text{Na}_2\text{O}, 3\text{Sb}_2\text{O}_5 + 10\text{H}_2\text{O}$; $\text{Na}_2\text{O}, 3\text{Sb}_2\text{O}_5 + 11\text{H}_2\text{O}$; $2\text{K}_2\text{O}, 3\text{Sb}_2\text{O}_5 + 10\text{H}_2\text{O}$; $\text{BaO}, \text{Sb}_2\text{O}_5 + 2\text{H}_2\text{O}$; $\text{BaO}, 3\text{Sb}_2\text{O}_5 + 5\text{H}_2\text{O}$; $9\text{BaO}, 10\text{Sb}_2\text{O}_5 + 18\text{H}_2\text{O}$; $2\text{CuO}, 3\text{Sb}_2\text{O}_5 + 10\text{H}_2\text{O}$; $\text{CuO}, 6\text{Sb}_2\text{O}_5 + 16\text{H}_2\text{O}$.

The antimonic acid described by Senderens (*Abstr.*, 1899, ii, 557) is believed to be a mixture of tri- and tetra-antimonic acids. N. L.

Sesquichlorides of Rhodium and Iridium. By ÉMILE LEIDIE (*Compt. rend.*, 1899, 129, 1249—1251).—Anhydrous rhodium sesquichloride is most conveniently prepared by dissolving in water the crude double salt, $\text{Rh}_2\text{Cl}_6, 6\text{NaCl}$, obtained by treating the metal with chlorine in the presence of sodium chloride, saturating the solution with hydrogen chloride, and after removing the precipitated sodium chloride, evaporating to dryness and heating the residue at $360\text{--}440^\circ$ in a stream of chlorine or hydrochloric acid. The anhydrous chloride forms a brown powder insoluble in water and acids; it dissolves in solutions of the alkalis, potassium cyanide, alkali tartrates, and oxalates. The double salts of iridium sesquichloride, $\text{Ir}_2\text{Cl}_6, 6\text{KCl} + 6\text{H}_2\text{O}$ and $\text{Ir}_2\text{Cl}_6, 6\text{NaCl} + 20\text{H}_2\text{O}$, are much more stable than the corresponding rhodium compounds, and are not completely decomposed even at 440° . The ammonium salt, $\text{Ir}_2\text{Cl}_6, 6\text{NH}_4\text{Cl} + 3\text{H}_2\text{O}$, like its rhodium analogue, undergoes a complex secondary reaction and cannot be employed in obtaining the sesquichloride. Iridium sesquichloride is best produced from the double salt, $\text{IrCl}_4, 2\text{NH}_4\text{Cl}$; it is a dark green substance insoluble in acids and alkalis. G. T. M.

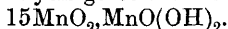
Mineralogical Chemistry.

Composition of Naphtha from Grosny. By K. W. CHARITSCHKOFF (*Chem. Centr.*, 1899, ii, 920; from *J. Russ. Chem. Soc.*, 1899, 31, 655—658. Compare this vol, i, 74).—The naphtha of Grosny contains thiophen in the proportion of about 1 part in 10,000,000 of "benzine," and mercaptan and thio-esters are also present. The decrease in sp. gr. of the "benzine" fraction is also assumed to indicate the presence of large quantities of isoheptane (*loc. cit.*). The fractions boiling at 29—30° have a composition corresponding with that of a mixture of two isomeric pentanes. By the action of nitrosulphuric acid on the fraction boiling at 82—89°, dinitrobenzene is formed, this compound being derived from tetrahydrobenzene. The Grosny naphtha contains the same compounds as American naphtha, but in different proportions. E. W. W.

Texas Petroleum. By F. C. THIELE (*Amer. Chem. J.*, 1899, 22, 489—493).—Petroleum from Corsicana and from Sour Lake, Texas, was submitted to fractional distillation. The results obtained show that the Corsicana oil is closely related to Pennsylvania oils, especially that of the Washington district, but it contains a certain amount of asphaltum, and hence care is necessary in distilling it. The greater part of the Sour Lake oil, which is a "surface oil," consists of oils excellently suited for lubricating purposes, the last fraction having a viscosity of 19° (Engler apparatus); it contains 20 per cent. of asphaltum. W. A. D.

Analyses of Moravian Minerals. By FRANTIŠEK KOVÁŘ (*Jahrb. f. Min.*, 1900, i, Ref. 25; from *Zeit. Chem. Ind. Prag.*, 1898, 4 pp.).—Graphite from Klein-Tressny contains, according to two determinations on different samples, 39·60 and 42·35 per cent. of carbon; the remainder is ash with about 1·5 per cent. of water.

Pyrolusite from Stěpánovitz occurs as nodules in red clay, which fills cavities in limestone; analysis gives the formula



Analyses are also given of dolomitic limestone and of a fireproof clay. L. J. S.

Magnetite from near Rome. By FERRUCCIO ZAMBONINI (*Jahrb. f. Min.*, 1900, i, Ref. 9; from *Rivista min. crist. ital.*, 1898, 21, 21—35).—A description is given of the fine crystals of magnetite occurring in lava at the quarries of Acquacetosa and Tavolato, near Rome. Sp. gr. 5·04—5·11. Analyses gave I for grains and II for crystals.

	Fe ₂ O ₃ .	FeO.	TiO ₂ .	MgO.	Total.
I.	69·5	28·7	0·9	0·7	99·8
II.	70·2	28·9	0·6	0·7	100·4

L. J. S.

Auriferous Cobalt Ores in the Transvaal. By H. OEHMICHEW (*Chem. Centr.*, 1899, ii, 788; from *Zeit. prakt. Geol.*, 1899, 271—274).—Auriferous smaltite occurs as veins in diabase at Kruis River and Laatsch Drift. L. J. S.

Fluorine in Swedish Phosphorites. By J. G. ANDERSSON and N. SAHLBOM (*Bull. Geol. Inst. Univ. Upsala*, 1899, (1898), 4, 79—87).—Analyses of phosphorites from various Swedish localities are given; some show the presence of fluorine in the proper proportion for fluorapatite. The phosphorites occur in fossiliferous strata and have been derived from organic remains. Analyses of fossil and recent brachiopod shells show them to consist largely of calcium phosphate with some fluorine.
L. J. S.

Analyses of Moravian Minerals. By FRANTIŠEK KOVÁŘ (*Jahrb. f. Min.*, 1900, i, Ref. 23; from *Chem. Blätter, Prag*, 1899, 4 pp.).—The minerals analysed are from Wür, near Bistritz. The primitive limestone gave I for the pure white, and II for the grey-white, variety.

	CaCO ₃ .	MgCO ₃ .	(Fe, Al) ₂ O ₃ .	Insol. in HCl.	H ₂ O.	Total.
I.	93·21	2·35	0·29	3·84	0·18	99·87
II.	92·08	3·16	0·70	3·98	0·24	100·16

A compact, white to bluish-grey substance resembling halloysite in appearance is shown by analysis III to be kaolinite.

Melinite [?] is compact, ochre-yellow and opaque; the fracture is earthy and the streak shining; analysis gave the results under IV, agreeing with the formula $H_4AlFeSi_2O_9$.

Sphene, as small honey-yellow crystals in the primitive limestone, gave V.

	SiO ₂ .	TiO ₂ .	Al ₂ O ₃ .	Fe ₂ O ₃ .	FeO.	CaO.	MgO.	H ₂ O.	Total.	Sp. gr.
III.	45·72	—	38·80	0·29	—	0·90	0·18	14·36	100·25	2·03
IV.	46·30	—	26·42	15·32	—	0·25	—	12·08	100·37	2·17
V.	32·55	41·58	—	—	0·84	25·41	—	—	100·38	3·48

L. J. S.

Analyses of Moravian Minerals. By FRANTIŠEK KOVÁŘ (*Jahrb. f. Min.*, 1900, i, Ref. 24; from *Rozpravy České Akad. [Memoirs Bohemian Acad.]*, 1898, 7, class II, No. IX, 8pp.).—Limonite as a botryoidal coating, from near Gross-Tressny, gave analysis I.

Gymnite occurs as small veins in limestone at Gross-Tressny; it is yellow and has a resinous lustre; analysis II gives the formula $Mg_4Si_3O_{10} + 5H_2O$.

Turgite encrusts bog-iron-ore at Rovecín near Öls; it is black and has a dark red streak; analysis III (also MnO, 0·96; SO₃ trace) gives the usual formula, $2Fe_2O_3 + H_2O$.

Vivianite occurs as dark blue aggregates of minute needles in cavities of the bog-iron-ore at Rovecín. Analysis IV (also insoluble 0·97), gives the formula $18FeO, 3Fe_2O_3, 8P_2O_5 + 56H_2O$.

	P ₂ O ₅ .	SiO ₂ .	Al ₂ O ₃ .	Fe ₂ O ₃ .	FeO.	CaO.	MgO.	H ₂ O.	Total.	Sp. gr.
I.	1·32	2·43	0·17	81·73	—	0·37	—	13·75	99·77	3·172
II.	—	41·17	0·18	0·76	—	trace	36·32	21·46	99·89	1·972
III.	0·12	2·05	0·29	92·07	—	0·18	—	4·89	100·56	4·315
IV.	28·51	—	trace	12·04	32·70	trace	—	25·43	99·65	2·637

L. J. S.

Analyses of Moravian Minerals. By FRANTIŠEK KOVÁŘ (*Jahrb. f. Min.*, 1900, i, Ref. 24; from *Zeit. Chem. Ind. Prag*, 1898, 4 pp.).—Whitish-grey kaolinite ("Steinmark") from the graphite mines at Klein-Tressny gave I; formula $2R'''_2Si_3O_9 \cdot R''SiO_3 + 2H_2O$.

Straw-yellow saponite filling cavities in the kaolinite is a plastic substance which falls to powder when exposed to the air. Anal. II gives the formula $Al_2Si_2O_9 \cdot 9MgSiO_3 + 9H_2O$.

Dull-green celadonite occurs as veins in the kaolinite. Anal. III, formula $R'''_2Si_3O_9 \cdot 4R''SiO_3 + 5H_2O$.

	SiO ₂ .	Al ₂ O ₃ .	Fe ₂ O ₃ .	FeO.	CaO.	MgO.	(K,Na) ₂ O.	H ₂ O.	Total.	Sp. gr.
I.	57.74	28.50	1.56	—	2.07	2.35	3.21	5.06	100.49	2.428
II.	51.42	7.60	0.59	—	0.43	28.15	0.24	12.07	100.50	—
III.	47.52	5.14	9.01	21.33	1.77	1.14	3.18	10.49	99.58	2.796

L. J. S.

Solidification of Fused Silicates under High and Normal Pressure. By C. F. W. A. OETLING (*Zeit. Kryst. Min.*, 1899, 32, 179; from *Tsch. Min. Mitth.*, 1897, 17, 331—373).—Since natural magmas must in most cases have solidified under high pressures, several comparative experiments were made to observe the effect of pressure on the crystallisation of silicate fusions.

In the experiments, the following crystallised minerals were formed: corundum, graphite, magnetite, spinel, pyroxene, plagioclase, and melilite.

L. J. S.

Olivine from Latium. By FERRUCCIO ZAMBONINI (*Zeit. Kryst. Min.*, 1899, 32, 152—156).—A crystallographic description is given of olivine from the lavas, &c., of Latium. An analysis gave:

SiO ₂ .	FeO.	Al ₂ O ₃ .	MgO.	NiO.	Total.	Sp. gr.
40.39	8.81	0.35	49.73	0.12	99.40	3.41

L. J. S.

[Mineral Analyses.] By VASILE C. BUTUREANU (*Zeit. Kryst. Min.*, 1899, 32, 188; from *Bull. Soc. Sci. Bucaresti*, 1897, 6, 264—293).—The following mineral analyses are given in a petrological paper on the eruptive rocks of Suzeava: I, oligoclase from syenite; II, oligoclase-andesine from miascite; III, orthoclase from ditroite; IV, biotite from syenite; V, biotite from miascite; VI, hornblende from miascite; VII, sodalite from ditroite.

	SiO ₂ .	Al ₂ O ₃ .	Fe ₂ O ₃ .	FeO.	CaO.	MgO.	K ₂ O.	Na ₂ O.	Cl.	Loss on ignition.
I.	61.68	23.95	—	—	5.25	0.16	1.09	6.99	—	1.05
II.	60.28	22.40	—	—	1.17	0.09	6.37	8.44	—	1.61
III.	66.23	18.12	—	—	0.30	—	9.90	5.02	—	0.29
IV.	42.25	19.79	6.68	15.34	2.55	2.56	7.88	2.01	—	1.43
V.	34.66	12.55	15.47	21.37	1.39	1.59	8.56	2.24	—	2.62
VI.	37.19	13.38	—	29.36	10.98	3.03	2.65	2.25	—	1.08
VII.	38.99	32.85	—	—	0.80	—	0.86	24.57	0.14	1.78

L. J. S.

Two New Hydrosilicates. By FERRUCCIO ZAMBONINI (*Zeit. Kryst. Min.*, 1899, 32, 157—163).—*Müllerite*. This occurs as a yellowish-green coating on iron and manganese oxides from Nontron, Dept.

Dordogne, France. It is soft, compact and opaque, and resembles nontronite ($\text{Fe}_2\text{O}_3, 3\text{SiO}_2 + 5\text{H}_2\text{O}$) in appearance, but differs from this in the blowpipe reactions and in containing less water. The mean (I) of three analyses gives the formula $\text{Fe}_2\text{O}_3, 3\text{SiO}_2 + 2\text{H}_2\text{O}$. Some previous analyses of nontronite and other varieties of chloropal show considerable variations in composition. [The name mullerite is already in use.]

Melite. This is from Saalfeld, Thuringia, and forms an aggregate of imperfect prismatic crystals and stalactitic masses. It is bluish-brown, opaque and brittle; $\text{H}=3$. Analysis gave the results under II. Encrusting this mineral are small, snow-white spheres, which are shown by analysis III to be schrotterite. [The name melite is likely to be confused with mellite.]

	SiO_2 .	Fe_2O_3 .	Al_2O_3 .	CaO .	MgO .	MnO .	H_2O .	Total.	Sp.gr.
I.	48.82	35.88	4.30	—	0.35	0.63	9.66	99.64	1.97
II.	14.97	14.90	35.24	0.78	—	—	33.75	99.64	—
III.	12.56	0.81	43.77	0.95	—	—	41.56	99.65	2.18

L. J. S.

Analyses of Sandstone Concretions. By CHARLES C. MOORE (*Proc. Liverpool Geol. Soc.*, 1898, 8, 241—265).—Analyses are given of concretions in Bunter sandstone from West Cheshire. L. J. S.

Phyllades and Slates. By T. MELLARD READE and PHILIP HOLLAND (*Proc. Liverpool Geol. Soc.*, 1898, 8, 274—293).—The phyllades of the Ardennes are compared with the slates of North Wales; several analyses of these, and of slates from other localities, are given.

L. J. S.

Vanadium in Rocks. By J. H. L. VOGT (*Chem. Centr.*, 1899, ii, 783; from *Zeit. prakt. Geol.*, 1899, 274—277).—From Hillebrand's analyses (*Abstr.*, 1899, ii, 112), the average amount of vanadium in the earth's crust is calculated to be between 0.0025 and 0.005 per cent.

L. J. S.

Rocks from Sumatra. By LUDWIG MILCH (*Chem. Centr.*, 1899, ii, 789; from *Zeit. Deutsch. geol. Ges.*, 1899, 51, 62—74).—In a paper describing the recent volcanic rocks of the Battak table-land in Central Sumatra, the following analyses by W. Herz are given: I, liparite; II, dacite; III, quartz-trachyte-andesite; IV, trachyte-andesite.

	SiO_2 .	Al_2O_3 .	Fe_2O_3 .	FeO .	CaO .	MgO .	K_2O .	Na_2O .	H_2O .	Total.
I.	71.25	14.21	0.85	0.43	2.72	0.89	6.74	3.11	0.48	100.68
II.	66.71	15.82	0.71	0.32	3.92	2.05	2.42	7.12	1.01	100.08
III.	69.44	15.21	1.74	0.56	1.99	0.93	4.53	5.11	0.77	100.28
IV.	60.41	17.44	1.98	1.78	2.79	1.85	5.64	7.51	0.51	99.91

L. J. S.

Meteoric Iron from Iredell, Texas. By WARREN M. FOOTE (*Amer. J. Sci.*, 1899, [iv], 8, 415—416).—This iron, originally weighing about three pounds, was found in 1898 near Iredell, Bosque Co., Texas. It differs from other Texas irons in the fine pitting and the absence of Widmanstätten figures on an etched sur-

face. Analysis by J. E. Whitfield of material partially freed from schreibersite gave :

Fe.	Ni.	Co.	P.	S.	Total
93.75	5.51	0.52	0.20	0.06	100.04

L. J. S.

Analyses of Glacial Deposits and Waters. By PHILIP HOLLAND and EDMUND DICKSON (*Proc. Liverpool Geol. Soc.*, 1898, 8, 130—150).—Analyses are given of mud and other glacial deposits and of glacial waters from the neighbourhood of the Varanger Fjord in Arctic Norway.

L. J. S.

Physiological Chemistry.

Influence of some Alcohols of Simple or Complex Function on the Digestion of Proteids by Pepsin or Trypsin. By E. LABORDE (*J. Pharm.*, 1899, [vi], 10, 484—488).—The influence on peptic and pancreatic digestion of the presence of 0·5 and 2 per cent. of alcohol and other substances was determined by digesting coagulated albumin with pepsin or trypsin for 3—4 hours at 40°, estimating the albumoses and peptones produced, and comparing the results with those obtained in blank experiments carried out under similar conditions. Peptic digestion appears to be favoured by small quantities of isobutyl alcohol, glycerol, and malic acid, and also, although very slightly, by methyl alcohol, whilst ethyl and propyl alcohols, lactic and tartaric acids, mannitol and dextrose distinctly retard digestion. Pancreatic digestion is aided by methyl and isobutyl alcohols, glycerol and dextrose, whilst a retarding action is exhibited by ethyl and propyl alcohols, lactic, malic, and tartaric acids, and mannitol. N. L.

Proteid Metabolism. By A. ALBU (*Chem., Centr.*, 1899, ii, 395; from *Forts. Med.*, 17, 505—508).—Caseon, the name given to a preparation of milk-proteid, is recommended in cases of malnutrition. Its absorption and utilisation compare favourably with those of other proteids. By giving a high percentage of proteid in the diet, a person can hold back proteid in the body, so that at the end of the research he is not in nitrogenous equilibrium, although the increase of body weight is not correspondingly high. W. D. H.

Nitrogenous Metabolism in the Cat. By LAFAYETTE B. MENDEL and ERNEST W. BROWN (*Amer. J. Physiol.*, 1900, 3, 261—270).—Kynurenic acid is not excreted by the cat even during the increased proteid metabolism produced by the administration of phloridzin. The ingestion of thymus and pancreas causes a marked increase of the uric acid output as in man and dog. Excretion of allantoin is also observed after thymus and pancreas feeding or after uric acid

ingestion; it was not observed after administration of hydrazine sulphate. The ordinary daily uric acid output per kilo. of body weight in the cat is scarcely smaller than in man and dog. Creatinine is ordinarily present in cat's urine in noticeable quantity.

W. D. H.

Comparative Determinations of the Specific Gravity, Dry Residue, and Amount of Iron in Blood. By S. JELLINEK and FR. SCHIFFER (*Chem. Centr.*, 1899, ii, 721; from *Wien klin. Woch.*, 12, 802—805).—Ordinary healthy blood has a sp. gr. 1·060—1·065, leaves 22·26—23·94 per cent. of dry residue, and contains 0·0431—0·0527 per cent. of iron. The iron was estimated by the ferrometer. The blood of patients suffering from various diseases was also examined. The various constants of the blood of healthy beings were found to maintain a certain relationship, and in other cases the sp. gr. and percentage of dry residue seemed also to be connected.

E. W. W.

Cerebro-spinal Fluid. By THEODOR PANZER (*Chem. Centr.*, 1889, ii, 722; from *Wien klin. Woch.*, 12, 805—807. Compare Nawratzki, *Abstr.*, 1898, ii, 36).—The cerebro-spinal fluids of two children had sp. gr. 1·0086 and 1·00917 respectively, and were faintly alkaline; the latter contained a hexose. Both fluids contained cholesterol, neutral fat and soaps, but albumoses, peptones, enzymes, and urea were not present in either. The fluid of the lower sp. gr. was found to contain 15·97 grams of solid substances, 7·34 of organic compounds, 8·63 of mineral substances, 1·404 of nitrogen, 5·99 of proteid substances (total), 4·85 of albumin, and 1·14 of globulin per litre. Analyses of both fluids are given.

E. W. W.

Hydrocele Fluid. By VERTUN (*Chem. Centr.*, 1899, ii, 624; from *Centr. Med. Wiss.*, 37, 529—530).—A specimen of hydrocele fluid was slightly opalescent, faintly alkaline, and contained traces of sodium chloride and phosphates, and 0·04 per cent. of proteid, which was mainly albumin, with a trace of globulin. Proteoses and spermin were absent. By the addition of Florence's potassium iodide solution, no crystals were formed; choline, which gives Florence's reaction as well as spermin, was therefore absent.

W. D. H.

Iodine in the Thymus and Thyroid. By LAFAYETTE B. MENDEL (*Amer. J. Physiol.*, 1900, 3, 285—290).—The accessory thyroids in man may contain relatively and absolutely more iodine than the thyroid proper of the same individual. The observations that the thyroids of newly-born children contain no iodine are confirmed. There is no satisfactory evidence to show that the carefully isolated thymus of man or animals contains iodine; traces found by others may have been due to adherent thyroidal tissue. The favourable effect of thyroid feeding in disease, like the similar effect of thymus, appears to be due not so much to the iodine as to organic substances with which it is united.

W. D. H.

Normal Existence of Arsenic in Animals and its Localisation in Certain Organs. By ARMAND GAUTIER (*Compt. rend.*, 1899, 129, 929—936).—A number of organs of different animals have been

examined for the presence of arsenic, small quantities of which were found in all the normal thyroid glands analysed; smaller proportions of this element also exist in the thymus and brain, and traces only in the skin. 127 grams of human thyroid gland gave 0.95 mg. of arsenic.

On separating the nucleins from the peptones of the thyroid gland of a sheep, all the arsenic was found in the nucleins; this points to the existence of arsenical nucleins along with those containing phosphorus.

In the following organs, arsenic could not be detected by the method of analysis employed (see this vol., ii, 168): sheep's, dog's, calf's and pig's liver, dog's and ox's spleen, pig's kidney, dog's flesh, pig's blood, and the human testicle. T. H. P.

Fat in Glands during Inanition. By R. NIKOLAIDES (*Chem. Centr.* 1899, ii, 485; from *Arch. Anat. Physiol.*, 1899, 518—523).—Considerable importance is attached to the presence of fat in gland cells. In glands like the dog's submaxillary gland, they are present only in the albuminous acini. They arise from protoplasm by metabolic action, and disappear during inanition. W. D. H.

The Source of Milk Fat. By WILHELM CASPARI (*Chem. Centr.*, 1899, ii, 483; from *Arch. Anat. Phys.*, 1899, Suppl., 267—280).—Even if it is shown that abundant proteid food increases the fat in milk, it does not follow that the fat originates from the proteid of the food. An important part of it is believed to originate from the fat of the food. Certainly iodised fats in the food pass into the milk, even though the food is poor in fat and rich in carbohydrates. W. D. H.

Formation of Acetone in the Body. By WALDVOGEL (*Chem. Centr.*, 1899, ii, 396; from *Centr. inn. Med.*, 20, 729—731).—The question is undecided whether acetone comes from the proteid of the food or of the body. Administration of thyroid increases the amount of acetone, but not of uric acid, in the urine. Carbohydrates lessen the formation of acetone, if given by the mouth, but not if given subcutaneously. Fat given by the mouth increases the acetone. Rabbits and dogs excrete quite different decomposition products of fat. Acetone, acetoacetic acid, and β -hydroxybutyric acid are considered to be the result of the oxidising power of the organism. W. D. H.

The Decomposition and Formation of Uric Acid in the Body. By HUGO WIENER (*Chem. Centr.*, 1899, ii, 262; from *Arch. exp. Path. Pharm.*, 42, 374—398).—Uric acid in the body of the rabbit leads to an increase of glycocine; this might occur by oxidation and hydrolysis with formation of allantoin and hydantoin as intermediate substances; but the experiments on animals do not confirm this. Neither can uroxamic acid or alloxan, which are highly toxic to rabbits, be regarded as intermediate substances. Extracts of the liver of dog or pig, but not of the ox, destroy uric acid; extracts of the kidney of ox and horse, but not of the dog, do so also. As uric acid can be destroyed in the body, the amount excreted in the urine in disease can be no measure of the amount produced. Glycocine is formed when uric acid is destroyed by extracts of ox kidney, but not

in so large amount as to account for all the uric acid ; the muscles of the ox give the same result. The 'surviving' ox liver is able, not only to destroy, but also to form uric acid from xanthine derivatives.

W. D. H.

Fate of Proteids after their Introduction into the Circulation. By IMMANUEL MUNK and MAX LEWANDOWSKY (*Chem. Centr.*, 1899, ii, 484 ; from *Arch. Anat. Phys.*, 1899, Suppl., 73—88).—In contradiction of Neumeister's results, it was found that if caseinogen, dissolved in soda, is introduced into the blood of rabbits (2.4 grams per kilo. of body weight), all but a small fraction is kept within the body and utilised. Egg-albumin is similarly used, in rabbits to the extent of 54 and in dogs of 82 per cent. Acid albumin, alkali-albumin, and nucleo-proteid are utilisable in a corresponding way. Proteids which have been profoundly altered, for instance, casein, are not utilised.

W. D. H.

Fate of 8-Hydroxyquinoline ; Excretion of Ethereal Hydrogen Sulphates ; Composition of Quinosol. By E. ROST (*Chem. Centr.* 1899, ii, 396 ; from *Arch. Kais. Ges. A.*, 15, 288—301).—Experiments on dogs show that 8-hydroxyquinoline leaves the body as the sulphate, and probably also as quinoline. When the amount of hydrochloric acid in the stomach is lessened, intestinal putrefaction increases, and so the amount of ethereal hydrogen sulphates in the urine rises. In complete inanition, the amount falls, but never to zero. Quinosol appears to be a mixture of 8-hydroxyquinoline sulphate and potassium sulphate.

W. D. H.

Chemical Reaction of the Intestinal Contents. By BENJAMIN MOORE and T. J. BERGIN (*Amer. J. Physiol.*, 1900, 3, 316—325).—The acid reaction of the intestinal contents to phenolphthalein is probably due to an excess of dissolved carbon dioxide. The alkaline reaction to methyl-orange, lacmoid, and litmus shows the absence of hydrochloric acid, and of all stronger organic acids, such as acetic, lactic, or butyric, which would be formed by the bacterial decomposition of carbohydrates or fats. These results were obtained by experiments on dog, sheep, and calf.

Absorption of food-stuffs, at least, in the dog, can be practically completed in the small intestine. A proteolytic enzyme active in alkaline solution, and a diastatic enzyme, also active in an alkaline solution, are present in the dog's intestine at this level.

W. D. H.

Cryoscopy of Urine in Diagnosis and Prognosis. By H. CLAUDE and V. BALTHAZARD (*Compt. rend.*, 1899, 129, 847—850).—If the difference between the freezing point of urine and that of water is corrected for the reduction due to soluble chlorides, and also, if necessary, for that due to sugar and albumin, the value δ thus obtained is a measure of the number of molecules, per unit volume of urine, of other compounds elaborated by the organism, and if this value is multiplied by the volume, V , of urine excreted in 24 hours and divided by the weight, P , in kilograms of the fixed proteids of the individual, the expression $\delta V/P$ has a value which varies greatly in different cases, and may serve as a valuable indication of

the beginning or progress of disease, especially in the case of maladies which affect the kidneys. C. H. B.

Origin of the Proteids in Albuminuria. By MAX CLOËTTA (*Chem. Centr.*, 1899, i, 267; from *Arch. exp. Path. Pharm.*, 42, 453—466).—The proportion of serum-albumin to serum-globulin in the urine in cases of albuminuria is very different from that in the blood. This is accounted for by the different permeability of membranes to the two proteids. Nucleo-proteid, which is stated to be absent from blood-serum, is considered to arise from the kidney tissue. W. D. H.

Sugar Formation in Severe Cases of Diabetes. By EMIL ROSENQVIST (*Chem. Centr.*, 1899, ii, 450—451; from *Berlin klin. Woch.*, 36, 612—617).—Partly on experimental, and partly on theoretical, grounds, the views of Seegen and Rumpf (*ibid.*, 36, 155), that in severe cases of diabetes mellitus fat may be a source of the sugar, is regarded as a possibility. W. D. H.

Hydroxybutyric Acid and its Relationship to Diabetic Coma. By ADOLF MAGNUS-LEVY (*Chem. Centr.*, 1899, ii, 63—64; from *Arch. exp. Path. Pharm.*, 42, 149—237).—The amount of hydroxybutyric acid in the urine of severe cases of diabetes without coma is from 0.5 to 1 per cent. In coma, 160 grams may be excreted daily, especially if sodium hydrogen carbonate is administered. Diabetic coma is regarded as acid poisoning, but probably the production of the acid is the result of toxin poisoning. In coma, as a rule, there is no rise of proteid katabolism, although doubtless the acid originates from proteid. In urines which contain acetone, but are not diabetic, as much as 7 grams of hydroxybutyric acid may be excreted daily. W. D. H.

Excretion and Detection of Glycuronic Acid in the Urine. By PAUL MAYER (*Chem. Centr.*, 1899, ii, 450; from *Berlin klin. Woch.*, 36, 591—593, 617—619).—The urine of a morphine-maniac contained glycuronic acid in combination, but the compound was not isolated. The greater number of tests for glycuronic acid are also given by pentoses, but if the orcinol test for pentoses is negative, and the urine contains glycuronic acid, a reducing substance will be obtained after treatment with sulphuric acid. Combinations of glycuronic acid do not yield a phenylhydrazine compound, but after treatment with sulphuric acid they do; the compounds are probably numerous, varying in melting point from 135° to 205°.

Glycuronic acid also occurs in urine after the use of chloral hydrate, and in small quantities in normal urine. W. D. H.

Excretion of Alloxuric Substances in Nephritis. By CHARLES F. MARTIN (*Chem. Centr.*, 1899, ii, 266; from *Centr. inn. Med.*, 20, 625—631).—From observations on seven cases of different forms of nephritis, it is found that the total alloxuric substances excreted in the day are diminished, but the relation of the alloxuric bases to uric acid is but little altered. W. D. H.

Theory of Narcosis. I. By HANS MEYER (*Chem. Centr.*, 1899, ii, 64; from *Arch. exp. Path. Pharm.*, 42, 109—118). II. By FRITZ BAUM (*Chem. Centr.*, 1899, ii, 65, from *ibid.*, 119—137).—In reference to Dubois' work on the action of anæsthetics (*Compt. rend. Soc. Biol.*, 1884, 583), the theory is advanced that the relative strength of these substances is dependent on their mechanical affinity for fatty substances (like lecithin in protoplasm), on the one hand, and to other constituents of protoplasm, especially water, on the other. In support of this view, the second paper shows that the proportion between concentration in fat and concentration in water of a number of narcotics runs parallel with their anæsthetising activity.

W. D. H.

Physiological Action of Creatine and Creatinine and their Value in Nutrition. By JOHN W. MALLET (*Chem. Centr.*, 1899, ii, 563; from *Bull. No. 66, U.S. Dept. Agric.*; and *Chem. News*, 80, 43—45, 54—56, 69—71, 77—78).—Almost the whole of the creatine and of the creatinine given to human beings is excreted as creatinine in the urine; the fæces contain none. These bases do not therefore serve for the building up of proteids. They are not, however, intermediate substances between proteid and urea, and it is not probable that these bases in muscle are changed even slowly into urea. This supports the view so often urged by physiologists that meat extracts have no nutritive value. The physiological action of creatine and creatinine is much weaker than commonly supposed.

W. D. H.

Rôle of Leucocytes in Poisoning by Compounds of Arsenic. By BESREDKA (*Ann. de l'Inst. Pasteur*, 1899, 13, 49—66, 209—224, 465—479).—The leucocytes are capable of engulfing toxic substances, among them various compounds of arsenic, arsenic trisulphide and arsenious acid being specially investigated. Leucocytosis is one result of the injection, but the healthy state, as well as the number of the leucocytes, is important. After traversing the leucocytes, the metal is ultimately eliminated by the urine. If positive chemiotaxis and leucocytosis do not occur, the animal dies; if they do, it is protected. The administration of previous small doses renders the animal immune to fatal doses. The *antiarsenin* present in the serum is probably not a compound of arsenic. The intermediate rôle of the leucocytic action is, however, essential in the antagonism.

W. D. H.

Action of the Tetanus Toxin on Nervous Substance. By JEAN DANYSZ (*Ann. de l'Inst. Pasteur*, 1899, 13, 156—168).—The nervous tissues fix to some extent the tetanus toxin, but this is not permanent, for *in vitro*, and probably *in vivo*, the toxin is again liberated by suitable media like physiological saline solution. The insoluble materials of the nervous tissue possess this power to the greatest degree, and the toxin is thus in part neutralised, but a determination of how much is rendered impossible by the fact that the soluble constituents of the tissue increase the toxic action.

W. D. H.

Fungus Poisons which Decompose Blood. By RUDOLF KOBERT (*Chem. Centr.*, 1899, ii, 781; from *Sitzungsber. naturf. Ges. Rostock*, 1899, No. 5).—*Agaricus phalloides* contains at least two poisons, con-

sisting of an alkaloid and a toxalbumin. When the alkaloid, which is soluble in alcohol but insoluble in ether, is administered to rabbits or cats, neither decomposition of the blood nor fatty degeneration of the organs takes place. The toxalbumin *phallin* has a stronger action than helvellic acid, but resembles it in dissolving the red corpuscles of the blood, dissolved oxyhæmoglobin, glycerophosphoric acid, and fragments of stroma also taking part in the action. By the liberation of glycerophosphoric acid, the alkalescence of the blood is decreased, the soluble hæmoglobin partially converted into methæmoglobin, and cyanose formed. A solution of phallin in 100,000 parts of water is sufficient to show the dissolving action on the red blood-corpuscles. Sections obtained from animals which had been poisoned by phallin showed many exudations of blood into the various organs. In many cases, the blood and urine were found to contain methæmoglobin or bile-colouring matters, and in most cases the kidneys were greatly affected. Phallin could not be detected in mushrooms or other edible fungi.

E. W. W.

Chemistry of Vegetable Physiology and Agriculture.

Buchner's Yeast Extract. By AUGUSTIN WRÓBLEWSKI (*Chem. Centr.*, 1899, ii, 672—673; from *Centr. Physiol.*, 13, 284—297. Compare Abstr., 1899, ii, 170).—The extract from a pure culture of wine yeast resembles that of ordinary yeast, both in composition and properties and, like it, is capable of fermenting sugar. The fermenting power of the zymase of the extract obtained from a pure culture of beer yeast is destroyed by the presence of formalin; 0·07 per cent. of hydroxylamine hydrochloride also exerts a slight preventive action, and larger quantities completely inhibit fermentation. From the results of experiments with pure hydrochloric acid, it is evident that the hydroxylamine hydrochloride combines with certain constituents of the extract, liberating hydrochloric acid, which then attacks the zymase. The extract has a denitrifying action on sugar solutions containing nitrites, and liberates nitrogen, but not carbon dioxide. Since the yeast cells are killed by even small quantities of nitrites, denitrification cannot be attributed to their action. The reduction of nitrites in soil is a purely chemical process, depending on their action on compounds analogous to amino-compounds, the action of small organisms being only of secondary importance. Nitrates are neither affected by the yeast nor its extract, and, like sodium chloride and ammonium sulphate, only hinder fermentation when present in large quantities. The addition of small quantities of neutral salts appears to increase the fermenting action of the yeast or of its extract, but large quantities of alcohol hinder fermentation, probably by precipitating the proteids of the extract.

The invertin resembles the proteose and peptone-like constituents of the extract, for when the extract is saturated with ammonium sulphate only a portion of the invertin is carried down mechanically, the major portion remaining in the filtrate. Invertin may be purified by fractionally precipitating with acetic acid, and finally fractionally precipitating from the acetic acid solution by means of alcohol. The inverting action of the invertin is increased by dilute acetic acid, and even a 4 per cent. solution of the acid does not very seriously interfere with this action. A 0.28 per cent. solution of hydrochloric acid does not appreciably affect the inverting power of invertin, but the prolonged action of alcohol, or the presence of even dilute solutions of alkalis, destroys it.

The properties of the zymase do not resemble those of the enzymes contained in the extract, and the former substance is more allied to protoplasm than to the group of proteoses and peptones. Zymase, unlike the enzymes, is unable to pass through an earthenware cell, and ferments only in concentrated solutions, dilution of the extract causing a rapid decrease of fermentation. Fermentation is also promoted by the addition of 1.5 per cent. of neutral salts. The enzymes, on the other hand, work better in dilute solutions and without the addition of salts. The effect of dilution and of the addition of neutral salts on the fermenting action of zymase appears to depend on osmotic processes. E. W. W.

[A Beer Disease.] By VAN LAER (*Compt. rend.*, 1900, 130, 53—56).—Beers termed by Belgian brewers "double face" or "*tweeskinde*" are quite clear by transmitted light, but by reflected light are dull brown and opalescent. Viewed from above, they appear dirty white and opaque, with a yellow fluorescence. This malady is closely connected with viscous fermentation, and seems due to a special organism, *Bacillus viscosus bruxellensis*, which always makes beer worts ropy; its development is promoted by the presence of nitrogenous compounds, but its effects are reduced if the liquid is thoroughly aerated. The bacillus converts carbohydrates into lactic, acetic, and butyric acids, either by consuming them directly, or by first converting them into gummy substances. Other conditions being equal, dextrose is first attacked and then saccharose, maltose, and lactose. No invert sugar is formed. C. H. B.

Reactions to Stimuli in Unicellular Organisms. By HERBERT S. JENNINGS (*Amer. J. Physiol.*, 1900, 3, 229—260. Compare Abstr., 1899, ii, 440).—This is a continuation of previous work in which *Paramecium* was used. It has been extended to *Chilomonas* and other flagellates, and also to numerous ciliated infusorians. The main results confirm those previously reached. Some of the results are now rather differently interpreted in accordance with modern chemical doctrines of solutions. W. D. H.

Effect of Ions on Flagellated Infusoria. By WALTER E. GARREY (*Amer. J. Physiol.*, 1900, 3, 291—315).—*Chilomonas* was the organism selected as the subject of the experiment. The effect of

chemicals is analogous to those of other stimuli like light or galvanism. Whilst inorganic acids have equal effects if the ion concentration is the same, organic acids behave differently and the effect is greater than would be expected.

W. D. H.

Bacteriological Enzymes as a Cause of Immunity and their Healing Action in Infective Diseases. By RUDOLF EMMERICH and OSKAR LÖW (*Chem. Centr.*, 1899, ii, 135; from *Zeit. Hyg.*, 31, 1—65).—The enzymes secreted by various bacteria unite with the proteids of blood or of organs; the compounds so formed are termed *immunoproteidins*; the proteid of the leucocytes which unites with the enzyme of the pathogenic bacteria is termed *proteid*. The so-called agglutination is nothing but the first stage of the effect of the enzyme. There are also bacterial enzymes which are not only bactericidal, but also destroy toxins; thus *pyocyanase*, the enzyme of *Bacillus pyocyaneus*, destroys the deadly effect of the diphtheria toxin.

W. D. H.

Changes in the Mineral Constituents of the Seed during Germination. By GUSTAVE ANDRÉ (*Compt. rend.*, 1899, 129, 1262—1265).—A preliminary communication dealing with observations made on the variation of the mineral constituents of the Spanish bean (*Phaseolus multiflorus*) from the commencement of germination to the period at which the dry weight of the seedling is again equal to that of the seed. The weight of mineral substances is trebled, but the constituents do not vary to the same extent. The quantity of phosphoric acid remains fairly constant, and there is a slight increase in the total nitrogen.

As long as the plant feeds on its reserve materials, the amount of potash remains constant, but when the chlorophyllous functions develop, the weight of this constituent increases. The amounts of silica and lime present at the end of the period under observation are respectively 400 times and 17 times as great as the original quantities. The analytical results are arranged in tabular form.

G. T. M.

Chlorophyllous Assimilation induced by Sunlight filtered through Leaves. By ED. GRIFFON (*Compt. rend.*, 1899, 129, 1276—1278).—Timiriazeff found that whitelight, after passing through a chlorophyll solution, loses its power of inducing chlorophyllous assimilation.

The author finds that sunlight, after traversing a single leaf still induces the decomposition of carbon dioxide, but the action is considerably diminished, and with diffused light is almost negligible. The effect produced by sunlight after passing through two leaves is so feeble that the assimilative action is masked by respiration.

These results are chiefly due to the absorption of luminous radiations by chlorophyll, but protoplasm and the colourless parts of leaves also diminish the action; the effect of light filtered through bleached or chlorotic leaves is approximately half that due to direct sunlight.

G. T. M.

Amount of Sulphur in Plants. By SERGEI M. BOGDANOFF (*Chem. Centr.*, 1899, ii, 489; from *J. Russ. Phys. Chem. Soc.*, 31, 471—477).—Estimation of sulphuric acid in vegetable ashes gives incorrect results, as considerable loss of sulphur may take place during incineration. Liebig's method is very satisfactory, and when small amounts of potassium nitrate are employed the results are very exact.

Plants contain much more sulphur than is indicated in Wolff's tables, and it is believed that the amount of sulphuric acid in soil is of practical importance. In some Russian soils, certain crops gave considerably higher yields after manuring with sulphates.

N. H. J. M.

Hydrocyanic Acid in Vicia Seeds. By F. F. BRUYNING, jun., and J. VAN HAARST (*Rec. Trav. Chim.*, 1899, 18, 468—471).—Flour from the following species and varieties of *Vicia* contains hydrocyanic acid: *V. sativa*, *V. sativa* v. *dura*, *V. sativa* v. *flore alb.*, *V. sativa* v. *Bernayer*, *V. sativa* v. *Britannica*, *V. canadensis*, *V. hirsuta*, and *V. angustifolia*; these hence contain amygdalin or analogous substances. No hydrocyanic acid was detected in: *V. narbonensis*, *V. cracca*, *V. agrigentina*, *V. biennis*, *V. disperma*, *V. pannonica*, and *V. cassubica*.

500 grams of flour from *V. sativa* contained 0.004 gram of hydrocyanic acid, and after germination for three days, the quantity was 0.003 gram. In the case of *V. sativa Britannica* and *V. angustifolia*, the same weight of flour yielded 0.0008 and 0.027 gram of acid respectively.

T. H. P.

Presence of Mannocellulose in the Ligneous Tissues of Gymnosperms. By GABRIEL BERTRAND (*Compt. rend.*, 1899, 129, 1025—1028. Compare Abstr., 1879, 613).—The tissues of the gymnosperms contain practically no xylan, but mannocellulose is present in considerable amount. The yield of mannose (obtained from mannocellulose by hydrolysis) from conifers is from 10—15 per cent. of the wood taken. In the *Gnetaceæ*, a class intermediate between the gymnosperms and angiosperms, the amount of mannocellulose is very small, and in some cases *nil*.

H. R. LE S.

Presence of Formaldehyde in Plants. By GINO POLLACCI (*Chem. Centr.*, 1899, ii, 881—882; from *Boll. Chim. Farm.*, 38, 601—603).—When leaves which have been exposed to the light are macerated and distilled with water, the first portion of the distillate contains formaldehyde. This compound was detected by the violet coloration produced on adding a mixture of codeine and sulphuric acid. This mixture is extremely sensitive to formaldehyde and even more so to the polymeric formaldehyde which is formed when the aqueous solution is evaporated. Other aldehydes such as acetaldehyde, propaldehyde, butaldehyde, valeraldehyde, and benzaldehyde give a yellow, whilst vanillin and acetone form a green, coloration. The formation of a solid, white polymeride, by slowly evaporating the aqueous solution at the ordinary temperature, is also characteristic of formaldehyde. The presence of this aldehyde was also detected by

the following methods. (1) An aqueous solution of aniline gives a white precipitate with formaldehyde. (2) When the distillate containing formaldehyde is added to a dilute solution of benzophenol and a solution of 94 per cent. sulphuric acid then poured into the mixture, a red ring is formed at the surface of contact of the liquids. (3) When a twig with green leaves which has been exposed to light is placed in an aqueous carmine solution which has been decolorised by sulphurous acid, the leaves become violet after a time, whilst the solution itself remains colourless. Magenta decolorised by sulphurous acid gives a violet coloration with formaldehyde. (4) Ammoniacal silver nitrate solution is reduced. (5) Nessler's reagent test-paper is turned black; and (6) phenylmethylhydrazine gives a white precipitate with the distillate.

E. W. W.

The "Honey" of *Euonymus Japonica*. By LÉON MAQUENNE (*Bull. Soc. Chim.*, 1899, [iii], 21, 1082—1083).—The honey-like substance which is sometimes found in dry seasons at the extremities of the branches of *Euonymus Japonica* is an exudation of the cell contents due to the punctures of insects; it is at first of a syrupy consistence, but soon dries to a crystalline mass. It has a marked sweet taste and is very soluble in water. When concentrated by evaporation, the solution deposits crystals of dulcitol and leaves a brownish, syrupy residue in which dextrose and saccharic acid were detected.

N. L.

Lotus Corniculatus. By GIUSEPPE D'ANCONA (*Chem. Centr.*, 1899, ii, 590—591; from *Staz. sper. agrar. ital.*, 32, 274—287).—Analyses of two Italian specimens of *Lotus corniculatus* are given:

	Water.	Crude proteid.	Crude fat.	Crude fibre.	N-free extract.	Digestible nitrogen.	Ash.
1.	80.285	3.429	0.723	6.563	7.582	0.256	1.418
2.	76.489	3.730	0.872	8.113	8.859	0.312	1.937

The dry substance contained (1) 10.757 and (2) 11.233 per cent. of pentosans. The pure ash had the following percentage composition:

	K ₂ O.	Na ₂ O.	CaO.	MgO.	Fe ₂ O ₃ + Al ₂ O ₃ .	P ₂ O ₅ .	SO ₃ .	SiO ₂ .	Cl.
1.	21.954	7.405	24.969	5.082	3.637	10.026	4.915	20.781	0.884
2.	21.987	6.772	23.629	4.091	5.066	10.687	4.383	22.335	1.029

N. H. J. M.

Absorption of Soluble Salts by Plants. By EM. DEMOUSSY (*Ann. agron.*, 1899, 25, 497—548 and 561—607).—A detailed account of experiments already described (*Abstr.*, 1899, ii, 172 and 238), with an historical introduction.

With regard to nitrates, the nature of the base has no effect on absorption by plants when supplied singly, provided that the base is not toxic; lithium, barium, and strontium nitrates, for instance, are only taken up in very small quantities, and their injurious effect soon becomes evident.

The fact that although plants absorb non-toxic metals with equal readiness, the amounts of these metals found in plants vary very greatly is attributed partly to the composition of the media in which the plant lives, and partly to the selective powers of plants.

Calcium, unlike potassium, does not prevent absorption of sodium.

Plants growing in solutions containing the same amount of calcium as nitrate and as chloride respectively absorbed more calcium in the form of nitrate than as chloride, but the absorption of chlorine was greater than that of nitrogen, owing to its greater molecular weight ; 2 mols. of nitrogen were absorbed to 1 mol. of chlorine.

N. H. J. M.

Composition of the Branches of Pear Trees Removed by Regular Thinning. By NAPOLEONE PASSERINI (*Bied. Centr.*, 1899, 28, 780—781 ; from *Ricerche e. Esper. Istituto Agrar. Scandicci*, 1896—1897).—Branches (without leaves) cut from pear trees were found to have the following composition :

Water.	N.	Crude ash.	CO ₂ in crude ash	Per cent. in pure ash.								Na ₂ O, Cl, SiO ₂ , loss.
				K ₂ O.	CaO.	MgO.	Fe ₂ O ₃ .	P ₂ O ₅ .	SO ₃ .			
49.29	0.506	1.748	33.79	15.11	63.00	4.51	0.60	4.90	2.64	1.66	7.58	

In the case of old pear trees, it was found (average of twelve experiments) that 1381 kilograms of wood are cut yearly. The loss per annum is therefore as follows : N, 6.99 ; K₂O, 2.40 ; CaO, 10.02 ; MgO, 0.72 ; P₂O₅, 0.78, and SO₃, 0.42 grams in each tree. The soil for pear trees should be comparatively rich in lime, and requires nitrogenous and potash manures.

N. H. J. M.

Which Meadows should be Manured with Potash as well as with Basic Slag and Superphosphate? By JULIUS NESSLER (*Bied. Centr.*, 1899, 28, 737—738 ; from *Woch. Landw. Ver. Baden*, 1899, No. 11, 139).—Level meadows, the soil of which is poor in potash but not too shallow, with much moss, &c., should receive, in autumn or winter, kainite (6—8) and basic slag (3—4 cwt.), and each subsequent year 2—3 and 3—4 cwt. respectively of basic slag and kainite. In the case of heavy soils, superphosphate is usually preferred to basic slag, and potassium chloride (40 per cent.) is employed instead of kainite.

Sloping meadows should have more potash applied to the higher than to the lower portions, which in some cases do not require direct potash manuring. Irrigation with water from granite or gneiss generally renders application of potash unnecessary.

The best chemical method of ascertaining whether potash is needed is to determine the amount of potash in the hay ; the grass must be cut at the beginning of the flowering period and carefully dried. Estimating the potash in the soil takes longer and gives more uncertain results.

N. H. J. M.

Composition of *Molinia cœrulea* and *Carex Goodenoughii*. By HEINRICH IMMENDORFF (*Bied. Centr.*, 1899, 28, 772—774 ; from *Landw. Jahrb.*, 1898, 27, iv, 503).—The two plants are important constituents of the herbage of peat meadows which are insufficiently drained and manured, but are not much valued as cattle-food. The composition as hay (water = 15 per cent.) is as follows :

	Crude protein.	Digestible protein.	Amides.	Fat.	N-free extract.	Crude fibre.	Ash.
1. <i>Molinia cœrulea</i>	6.75	4.26	0.88	2.44	41.28	30.96	3.47
2. <i>Carex Goodenoughii</i>	9.00	4.69	0.50	2.51	42.14	27.40	3.94

Whilst *Molinia* hay is of very poor quality, the results obtained with *Carex* are more satisfactory, but the yield is very small. The dry substance of the two plants contained: Ash, (1) 4.196, (2) 4.64; K_2O , (1) 1.21, (2) 1.49; CaO , (1) 0.25, (2) 0.39; and P_2O_5 , (1) 0.29, (2) 0.43 per cent. N. H. J. M.

Hops and Hop Soils. By JOSEPH HANAMANN and LEOPOLD KOURINSKY (*Bied. Centr.*, 1899, 28, 778; from *Zeit. Landw. Versuchs.-wesen. Oesterr.*, 1898, 1, 411).—During the early periods of growth, hop plants require plenty of potash, phosphoric acid, and nitrogen; subsequently, the plants contain nearly as much lime as potash.

The leaves and tendrils are rich in lime, and in the assimilating organs 50 per cent. of the ash consists of lime, indicating considerable production of organic acids in the sap, which have to be neutralised with lime. The leaves contain much more potash, lime, magnesia, and phosphoric acid than the tendrils and stems, whilst the umbels contain the most potash and phosphoric acid.

In the original paper, analyses of the soil and of the ashes of hops at different periods of growth are given. N. H. J. M.

Influence of Potash on the Development of Sugar Beet. By JULIUS STOKLASA (*Chem. Centr.*, 1899, ii, 490; from *Zeit. Zucker-Ind. Böhm.*, 23, 493—501).—Results of field experiments showed that potassium sulphate considerably increased the yield of roots and the percentage of sugar. Potassium chloride, in conjunction with superphosphate and nitrate, also increased the yield of roots without injuriously affecting the percentage of sugar. N. H. J. M.

Assimilation by Sugar Beet and Estimation of Available Nutritive Matter in Arable Soil. By H. WILFARTH (*Chem. Centr.*, 1899, ii, 536—537; from *Zeit. Ver. Rübenzucker-Ind.*, 1899, 645—652).—Whilst sugar beet grows normally when manured with nitrate, ammonium salts and blood-meal gave decidedly unsatisfactory results.

Amides were determined in the roots as an indication of the degree of unripeness.

When calcium nitrate is employed as manure, the lime is eliminated from the root, whilst with potassium nitrate the potash is retained. Deficiency of nitrogen gives rise to yellow leaves, whilst a deficiency of potash produces brown and white spots on the leaves. In absence of sufficient phosphoric acid, the leaves do not become yellow as stated by Stoklasa, but their growth is checked, and they have a dark green colour with black edges and spots.

The results of pot experiments showed that with insufficient potash the roots contained only 4 parts of K_2O to 1000 parts of sugar, the amounts under normal conditions being 6—8 parts; with six times the necessary amount of potash, the roots were found to contain 37 parts of K_2O per 1000 of sugar. The roots are more liable to injury by nematodes in absence of potash than when a small amount of potash is applied.

It is proposed to estimate available plant constituents in soils by growing sugar beet, carrots or celery, and analysing the plants.

N. H. J. M.

Influence of the Amounts of Water and of Nutritive Substances in Soil on the Activity and Development of Potatoes. By JOHANN WILMS (*Chem. Centr.*, 1899, ii, 628; from *J. Landw.*, 47, 251—292).—The occasional injurious effect of Stassfurt salts on potatoes is attributed to the presence of potassium chloride. Nitrogenous substances are favourable to the development of the plants and to starch production. Potash also seems favourable to starch production. Increased amounts of moisture in the soil always diminish the percentage of starch in the tubers; and proportions of chlorides, which are otherwise harmless, become injurious when the amount of water is large. Transpiration is increased when the percentage of water in the soil increases, and there may be an increase, although less marked, in the actual amount of starch produced.

N. H. J. M.

How much Phosphoric Acid should good Arable Soil Contain? By AIMÉ PAGNOUL (*Ann. Agron.*, 1899, 25, 549—557).—The results of pot experiments, in which incarnate clover was grown in soils containing very little, and a good deal, of phosphoric acid respectively, with and without addition of superphosphate, indicated that 0.1 per cent., which is generally considered to be a normal amount for good soil, is too low, and that 0.15 to 0.2 per cent. is more probably the limit, at any rate for incarnate clover, beyond which manuring with phosphates becomes unnecessary. N. H. J. M.

Alinit. By W. KRÜGER and W. SCHNEIDEWIND (*Chem. Centr.*, 1899, ii, 628; from *Landw. Jahrb.*, 28, 579—591).—Experiments were made on the behaviour of alinit towards free atmospheric nitrogen in nutritive solutions containing nitrogenous matters, and also towards nitrates. It is concluded that the preparation is without practical value. The microbe does not nitrify, but there was production of nitrite.

N. H. J. M.

Composition of Green Manure grown on Peaty and on Sandy Soils. By HEINRICH IMMENDORFF (*Bied. Centr.*, 1899, 28, 726—733; from *Landw. Jahrb.*, 1898, 27, 503).—The composition as regards dry matter and nitrogen of the crops grown for green manure on peat land (yellow, blue, and white lupins, serradella, grey peas, beans, rape, and white mustard) scarcely differs from that of the same plants grown in ordinary soil. In absence, however, of inoculation, the percentage of nitrogen in the dry matter is liable to be very low. In the case of blue lupins, for instance, the nitrogen in the dry matter was (1, inoculated) 3.26 and (2, not inoculated) 1.98 per cent.

In light, sandy soils, the most suitable crops for green manuring are lupins and serradella (white mustard is quite unsuitable), and the composition of the plants is normal. Application of burnt lime (3,000 kilograms per hectare) was very beneficial, even in the case of lupins. The soil did not require inoculation.

Pot and field experiments were made to ascertain the amounts of organic matter and nitrogen in the above-ground growth and roots of serradella and lupins grown in peaty soil fully manured with minerals. Normal percentages of nitrogen, both in roots and in the growth

above-ground, were only obtained after inoculation. Lupins yield (in the roots) more organic matter than serradella, but the latter is more nitrogenous.

Crops of serradella and lupins the above-ground growth of which contain 100 and 140 kilograms of nitrogen per hectare, yield in the roots about 15 and 20 kilograms of nitrogen respectively; these amounts may undoubtedly be increased by deepening the soil.

N. H. J. M.

Testing Soils for Application of Commercial Fertilisers.
By H. A. WEBER (*J. Amer. Chem. Soc.*, 1899, 21, 1095—1099).—Five carefully selected portions of the soil are put into Wagner pots, and to four of these are added various descriptions of manure to ascertain which will answer best.

The seeds of the crops required to be raised are then introduced with the usual precautions and allowed to germinate; it is not necessary to bring the plants to maturity; observations made during 5 or 6 weeks will give sufficient information.

L. DE K.

Analytical Chemistry.

Estimation of Chlorine in Bleaching Powder. By C. WOŁOWSKI (*Zeit. anal. Chem.*, 1899, **38**, 711—713).—The hypochlorite solution is added from a burette to potassium iodide acidified with sulphuric acid. A number of mixtures are made in which the amount of iodide is the same, and by shaking each mixture with chloroform the point is ascertained at which enough chlorine has been added to convert all the iodine into trichloride, which of course does not colour the chloroform. The author prefers to work with only 5 milligrams of potassium iodide, and measures the hypochlorite solution by counting the drops.

M. J. S.

Separation of Chlorine and Iodine. By LUDWIG VANINO and O. HAUSER (*Ber.*, 1899, **32**, 3615—3617. Compare Abstr., 1898, ii, 545; and 1899, ii, 249).—Silver iodide, when heated at 90° with formaldehyde dissolved in 50 per cent. potassium hydroxide solution, is scarcely affected, whereas silver bromide under these conditions is almost wholly reduced, a considerable amount of reduction taking place even at the ordinary temperature; silver chloride is completely decomposed, even in the cold. When a mixture of silver chloride and iodide is heated at 40° with an alkaline formaldehyde solution of the above strength, the chloride is completely reduced, whilst the iodide remains unchanged; the precipitate is treated with nitric acid, the silver derived from the chloride dissolves, and is reconverted into the haloid salt. In this way, a quantitative separation of iodine and chlorine may be rapidly effected.

G. T. M.

Titration of Potassium Iodide. By E. VINCENT (*J. Pharm.*, 1899, [vi], 10, 481—483).—The valuation of potassium iodide may be rapidly and accurately effected by the following process, which avoids the errors incidental to some of the methods usually employed. A suitable quantity of the solution obtained by dissolving 1 gram of the sample in a litre of water is mixed with an equal volume of a 0.2 per cent. solution of iodic acid, and the liquid added from a burette to 5 or 10 c.c. of *N*/10 thiosulphate solution until a permanent yellow tint is produced. 0.2 per cent. of potassium hydrogen carbonate is added to the thiosulphate solution in order to prevent oxidation of the latter by the excess of iodic acid. N. L.

Estimation of [Dissolved] Oxygen in Water. By F. ZETSCHE (*Chem. Centr.*, 1899, ii, 727; from *Zeit. Unters. Nahr.-Genussm.*, 2, 696—697).—A glass-stoppered bottle of 250—300 c.c. capacity is filled completely with the water; 1 c.c. of a saturated solution of manganous sulphate is introduced at the bottom of the liquid by means of a pipette, followed by 2 c.c. of a solution containing 48 grams of sodium hydroxide and 15 grams of potassium iodide per 100 c.c. The whole is now thoroughly shaken, and when the manganous-manganic hydroxide has subsided, the stopper is removed, 5 c.c. of hydrochloric acid are introduced, the stopper is replaced, and the whole shaken until a clear solution is obtained. The liquid is then emptied into a beaker, and the liberated iodine titrated with *N*/100 solution of sodium thiosulphate. When calculating the result, 3 c.c. only must be deducted for the reagents added; the volume of the hydrochloric acid added does not affect the calculations. L. DE K.

Estimation of Sulphuric Acid in the Presence of Iron. By GRÉGOIRE N. WYROUBOFF (*Bull. Soc. Chim.*, 1899, [iii], 21, 1046—1049. Compare Abstr., 1899, ii, 329 and 611).—A criticism of the methods described by Küster and Thiel (Abstr., 1899, ii, 247). N. L.

Estimation of Nitrogen in Fertilisers containing Nitrates. By F. P. VEITCH (*J. Amer. Chem. Soc.*, 1899, ii, 1094—1095).—Fields' process is recommended with only a slight modification. To the nitrate, 35—40 c.c. of sulphuric acid containing 34 grams of salicylic acid per litre, and after it has dissolved, 6—7 grams of crushed potassium sulphide, are added. After first heating over a low flame for 15 minutes, the contents are boiled for 1½ hours, then cooled and distilled as usual with excess of soda. L. DE K.

Direct Estimation of Available Phosphoric Acid. By F. P. VEITCH (*J. Amer. Chem. Soc.*, 1899, 21, 1090—1094).—The sample is first extracted with water and the solution filtered into a 500 c.c. measure containing 5—10 c.c. of nitric acid. The insoluble residue is then treated with the ordinary ammonium citrate solution and the two liquids are united. The phosphoric acid is now precipitated in an aliquot part of the solution by means of the ordinary molybdate solution, the precipitation being probably complete in two hours at 65°. It does not seem necessary to destroy the citric acid, or any other organic matter present in the manure. L. DE K.

[Estimation of the Available Phosphoric Acid in Soil.] By AIME PAGNOUL (*Ann. Agron.*, 1899, 25, 554—557).—After determining the dry matter and calcium carbonate, an amount of soil containing 10 grams of dry matter is digested for 2 hours with a solution containing 120 grams of glacial acetic acid in 1 litre (10 c.c. plus the amount required to dissolve the calcium carbonate) diluted with water to 50 c.c., the whole being shaken twelve times during digestion. The phosphoric acid is then determined in 25 c.c. of the filtered extract, by means of the colour reaction produced by potassium ferrocyanide in very dilute phosphomolybdate solution. The solutions required are (1) ordinary ammonia, 100 c.c., diluted to 1 litre; (2) sulphuric acid, 70 or 80 c.c., diluted to 1 litre; (3) potassium ferrocyanide, 10 per cent.; and (4) a standard phosphomolybdate solution containing exactly 4 milligrams of phosphoric acid per litre. This is prepared by precipitating a solution of sodium or ammonium phosphate, containing 4 mg. of phosphoric acid, as phosphomolybdate in the usual manner, decanting over a small filter, and washing with nitric acid until the filtrate gives no coloration with ferrocyanide. The whole is then dissolved in the dilute ammonia (solution 1) and made up to 1 litre with the same dilute ammonia.

The phosphoric acid in 25 c.c. of extract (corresponding with 5 grams of soil) is determined by precipitating as phosphomolybdate, filtering, and redissolving the precipitate in the dilute ammonia. The volume of the solution (V) will be from 10—50 c.c., according to the amount of precipitate. 5 c.c. of the standard phosphomolybdate solution (containing $P_2O_5 = 0.02$ milligram) is next put into a tube 2 cm. wide and divided into c.c., 5 c.c. of the solution to be examined being put into a similar tube. After adding ferrocyanide solution (2 c.c.) to both tubes, dilute sulphuric acid (solution 2) is added drop by drop until a permanent brown tint is obtained. A few drops of water are added to the tube containing the standard solution to make the volume up to 10 c.c., whilst the liquid in the second tube is diluted until the tints of both are alike, and the volume (V') read off. The phosphoric acid, in mg. per cent., in the soil will be $0.4 \times \frac{V_1}{10} \times \frac{V}{5}$. If the colour

produced by 5 c.c. of solution is too dark, 1 or 2 c.c. may be employed, but the solution must then be diluted with the ammonia solution to 5 c.c. before adding the ferrocyanide. A number of determinations may be made simultaneously with advantage. N. H. J. M.

Detection of Fraudulent Additions to Bone Superphosphate. By HENRI LASNE (*Chem. Centr.*, 1899, ii, 973—974; from *Ann. chim. anal. app.*, 4, 235—331).—A microscopical examination will indicate the origin of added mineral phosphates, foreign minerals, &c.

To facilitate the microscopic research, the sample may be first freed from true bone phosphate by successive treatment with dilute (3 per cent.) acetic acid and a concentrated solution of ammonium citrate.

L. DE K.

Valuation of Basic Slags. By FRANZ W. DAFERT (*Chem. Centr.*, 1899, ii, 727; from *Zeit. Landw. Vers.-Wes. Oesterr.*, 2, 467—476).—The author states that the valuation of basic slags by their citrate

solubility cannot be considered a scientific method, as it depends too much on the personal equation of the operator. L. DE K.

Detection and Estimation of very small Quantities of Arsenic in the Organs. By ARMAND GAUTIER (*Compt. rend.*, 1899, 129, 936—938).—The method, details of which are given, consists essentially in destroying the organic matter by successive treatment with nitric acid, sulphuric acid, and, finally, nitric acid again; the arsenic is precipitated, together with an excess of sulphur, by hydrogen sulphide, the precipitate digested with ammonia to dissolve the arsenious sulphide, which is then oxidised by a mixture of nitric and sulphuric acids, and finally treated by Marsh's method for detecting arsenic. T. H. P

Estimation of Graphitic Carbon in Cast Iron and Pig Iron. By ALLEN P. FORD and IVAN M. BREGOWSKY (*J. Amer. Chem. Soc.*, 1899, 21, 1113—1115).—1 gram of the sample is dissolved in nitric acid of sp. gr. 1.2; a few drops of hydrofluoric acid are then added and the liquid boiled for a short time to dissolve the silicon. After diluting with four times the bulk of water, the insoluble matter is collected on a Gooch's crucible, the asbestos of which has been selected with care and purified by digestion in hydrochloric acid. After drying for fully an hour at 120°, the crucible is weighed, the graphite burnt off, and the crucible re-weighed, the difference representing the graphite. L. DE K.

Report of the [American] Committee on Coal Analysis. By WILLIAM A. NOYES, WILLIAM F. HILLEBRAND and CHARLES B. DUDLEY (*J. Amer. Chem. Soc.*, 1899, 21, 1116—1132. Compare Abstr., 1898, ii, 488).—Final instructions are given as to the analysis of coal so as to ensure uniform results. When estimating the sulphur, it is recommended to avoid the use of coal gas. If an ultimate analysis is thought desirable, the sample should be burnt with lead chromate so as to retain the sulphur; it is unnecessary to employ a spiral of copper. When calculating the percentage of oxygen, it is recommended to deduct from 100 the sum of the carbon, hydrogen, nitrogen, ash, and five-eighths of the sulphur. In the preliminary report, it was recommended to give the heating effect on the basis of the coal burned to "vapour of water at 100°;" this is now altered to "liquid water at the ordinary temperature." L. DE K.

Estimation of Volatile Combustible Matter in Coke and Anthracite Coal. By RICHARD K. MEADE and JAMES C. ATTIX (*J. Amer. Chem. Soc.*, 1899, 21, 1137—1145).—In order to completely expel the last portions of volatile matter from coke or anthracite, it is necessary to finally employ the blast, but this causes some of the carbon to burn; the oxidation may be practically prevented by heating in a current of nitrogen.

If after heating a sample over a blast, say, for 7 minutes and weighing, the ignition is continued for another 7 minutes under exactly the same conditions, the second loss in weight should

represent with fair accuracy the amount of carbon oxidised during the first heating. The results obtained by this correction are satisfactory.

L. DE K.

Apparatus for the Analysis of Illuminating and Fuel Gases. By GEORGE E. THOMAS (*J. Amer. Chem. Soc.*, 1899, 21, 1108—1112).—This is a compact apparatus for technical work. It consists essentially of a burette and levelling tube joined by rubber and capillary glass tubes to a series of absorbing bottles, filled with aqueous caustic potash, bromine water, and phosphorus covered with water, another bottle is filled with water only, as it is only used for storing gas.

There is also the usual arrangement for exploding mixtures of gas and air. The water in the burette is acidified with sulphuric acid so as to diminish the solubility of carbon dioxide.

L. DE K.

Chemical Detection of Carbonic Oxide in Blood. By KARL IPSEN (*Chem. Centr.*, 1899, ii, 889; from *Vierteljahrschr. gericht. Med. öffentl. Sanitätswes.*, [iii], 18, 46—65).—4—10 c.c. of the suspected blood is put into a small test-tube, a drop of caustic alkali is added, and then a small amount of dextrose. After closing the tube with cotton wool and sealing it with paraffin wax, it is well shaken and kept for some length of time in a cool place. A blank experiment should be made with pure blood at the same time.

Blood containing carbonic oxide turns a light cherry-red colour, whilst ordinary blood becomes almost black.

L. DE K.

Chemical Detection of Carbonic Oxide in Blood. By LEO WACHHOLZ (*Chem. Centr.*, 1899, ii, 889; from *Vierteljahrschr. gericht. Med. öffentl. Sanitätswes.*, [iii], 18, 255—257. Compare preceding abstract).—The dextrose test may lead to erroneous results. The best process at present in use for detecting carbonic oxide in blood is the tannic acid process, proposed by Kunkel and modified by Schulz.

L. DE K.

Apparatus for the Estimation of Carbon Dioxide in Mineral Waters. By ALFRED HELD (*Bull. Soc. Chim.*, 1899, [iii], 21, 983—986).—The essential feature of the apparatus lies in the fact that the precipitation of the carbon dioxide by milk of lime and calcium chloride, the collection and washing of the precipitate, and the decomposition of the latter by dilute acid, are carried out in one and the same vessel, in an atmosphere free from carbon dioxide. For this purpose, the flask, in which the precipitation has been effected in the usual manner, is fitted with a cork bored with three holes, through which are passed: (1) A delivery tube, serving both for the admission of air free from carbon dioxide, and, subsequently, for the passage to the absorption apparatus of the gas liberated from the precipitated carbonate; (2) a tap-funnel for the inlet of water or acid; (3) a syphon tube, one limb of which reaches nearly to the bottom of the flask, and is connected by a cork to a small test-tube, pierced with several holes, and covered with a cap of filter paper. By means of this syphon, the liquid and washings are removed from the flask, leaving the precipitate to be treated with acid in the usual way.

N. L.

Estimation of Carbon Dioxide in Ammoniacal Gas-Liquor. By F. CHEVALET (*Chem. Centr.*, 1899, ii, 847; from *Ann. chim. anal. appl.*, 4, 295—296).—The sample is allowed to run into an acid solution of cuprous chloride; the apparatus employed, which is a slight modification of the one introduced by Geissler, is weighed before and after the operation, and the carbon dioxide found by difference. The object of the copper solution is to retain hydrogen sulphide. L. DE K.

Stutzer and Hartleb's Process for the Estimation of Combined Carbon Dioxide (Calcium Carbonate) in Soils. By RUDOLF WOY (*Chem. Centr.*, 1889, ii, 847; from *Zeit. öffentl. Chem.*, 5, 400—401. Compare Abstr., 1899, ii, 521).—The author objects to the process, as decided quantities of ammonia are given off on boiling by the dissociation of the added ammonium chloride. L. DE K.

Estimation of Silver on Plated Copper Utensils. By JULIEN GIRARD (*Chem. Centr.*, 1899, ii, 975; from *Ann. chim. anal. appl.*, 4, 342—343).—The object is thoroughly cleansed and immersed in a liquid composed of 9 volumes of sulphuric and 1 volume of nitric acid; this rapidly dissolves the silver without acting appreciably on the copper. The silver may be ascertained from the loss in weight, or be estimated in the solution as chloride. L. DE K.

Estimation of Small Quantities of Zinc in Organic Substances, especially in Apple Chips. By KARL B. LEHMANN (*Zeit. anal. Chem.*, 1899, 38, 723; from *Arch. Hygiene*, 28, 291).—The substance is mixed with nitric acid and either incinerated until perfectly white, or after charring is mixed with sodium carbonate and potassium nitrate and fused in a porcelain basin. The ash is dissolved in nitric acid, copper precipitated by hydrogen sulphide, and the zinc then separated from iron, aluminium, and silica by repeated precipitation with ammonia. A small excess of acetic acid is added to the ammoniacal filtrate and the zinc thrown down by hydrogen sulphide. The zinc sulphide is then dissolved in hydrochloric acid and the zinc titrated by Fahlberg's ferrocyanide method (this Journ., 1875, 665) using a ferrocyanide solution of which 1 c.c. precipitates 0.1 milligram of zinc. The zinc solution must be only feebly acid; the presence of ammonium salts is harmless. For quantities of less than 1 milligram, a correction (about -0.15 mg.) must be applied. M. J. S.

Titrimetric Estimation of Cerium. By PHILIP E. BROWNING [with WM. D. CUTLER, G. A. HANFORD, LEO. A. LYNCH, and F. J. MALL] (*Zeit. anorg. Chim.*, 1899, 22, 297—307).—Accurate results are obtained with the following modification of Bunsen's method. The cerium dioxide is mixed in a stoppered flask with potassium iodide and a few drops of water, the air is then driven out by a current of carbon dioxide, pure hydrochloric acid added, and the flask stoppered and heated with steam for 1 hour, or until the dioxide is completely dissolved. The contents of the flask are then diluted, and the liberated iodine titrated with thiosulphate. The liberated iodine was also estimated by titration with arsenious acid after the contents of the

flask connected with an absorption apparatus were neutralised with potassium hydrogen carbonate, but in this case a loss of about 2 per cent. of the iodine occurred.

Cerium dioxide is only partially reduced by arsenious acid and cannot therefore be estimated by this reagent.

Stolba's method (Abstr., 1880, 749) by titrating the oxalate with permanganate, gives good results. A measured quantity of cerium chloride solution is precipitated with a known excess of ammonium oxalate and the precipitate separated by filtration and washed. The cerium oxalate is then dissolved in sulphuric acid and the oxalic acid titrated with permanganate. The excess of ammonium oxalate in the filtrate and wash-water is also titrated, the result giving a control to the titration of the cerium oxalate. E. C. R.

Preliminary Tests for Clays. By WERNER CRONQUIST (*Chem. Centr.*, 1899, ii, 974; from *Oesterr. Zeit. Berg-Hütt.*, 47, 522—525).—Clays intended for the manufacture of crucibles should contain at most 47—72 per cent. of sand. This may be estimated with sufficient accuracy by first boiling the clay with hydrochloric acid, and then boiling the undissolved matter with a strong solution of sodium carbonate. L. DE K.

Rapid Solution of Ignited Ferric Oxide in Hydrochloric Acid. By HUGO BORINTRAGER (*Zeit. anal. Chem.*, 1899, 38, 774).—By adding to the hydrochloric acid a little iron-free manganese dioxide, even strongly ignited ferric oxide can be dissolved with great facility. This effect seems to be due to the chlorine evolved, since all the halogens facilitate the solution of ferric oxide in hydrochloric acid. M. J. S.

Use of Hydrogen Peroxide in Quantitative Analysis. By CARL FRIEDHEIM and ERNST BRÜHL (*Zeit. anal. Chem.*, 1899, 38, 681—710).—After a review of the various proposals that have been made for the use of hydrogen peroxide in qualitative and quantitative reactions, the greater part of the paper is devoted to a study of the methods advocated by Jannasch and his pupils; separation of manganese from copper, zinc, and nickel, and of chromium from iron, aluminium, and manganese, by means of alkaline solutions of the peroxide (Abstr., 1895, ii, 331; 1896, ii, 220, 222, 546, 548). It is shown that the apparently satisfactory results obtained by Jannasch are largely due to compensating errors, none of the above separations being at all complete. The accuracy of the method of estimating manganese, in the absence of other metals, by precipitation with ammonia and hydrogen peroxide (Rosenthal, Abstr., 1887, ii, 923) is fully confirmed, but only in the absence of any considerable amount of ammoniacal salts. With increase in the proportion of ammonium salts, the amount of unprecipitated manganese increases, but at the same time the precipitate becomes more highly oxidised, so that apparently correct results may in some cases be obtained if the precipitate is regarded as Mn_3O_4 . Although alkaline solutions of

chromic oxide are oxidised by hydrogen peroxide, the oxidation is under no circumstances complete. This probably is the reason why chromium cannot by this method be separated from metals whose hydroxides are insoluble in alkalis. M. J. S.

Estimation of Thallium as Chromate. By PHILIP E. BROWNING and GEORGE P. HUTCHINS (*Amer. J. Sci.*, 1899, [iv], 8, 460—462).—Crookes having shown that thallous chromate is practically insoluble in water, the authors have applied this principle to the gravimetric estimation of thallium. The liquid containing the thallium is rendered distinctly alkaline by adding a solution of potassium carbonate, then heated to 80°, and precipitated with excess of potassium dichromate. The thallous chromate is collected on a Gooch's asbestos filter, washed, dried over a low flame, and weighed. Twelve test experiments prove the accuracy of the method. If precipitated in the cold, the precipitate is liable to run through the filter; this may be largely prevented by adding ammonium nitrate.

Moderately accurate results may be obtained by adding a known amount of potassium dichromate and titrating the excess with arsenious acid as described by Browning (*Abstr.*, 1899, ii, 73). L. DE K.

Ultimate Analysis of Organic Compounds. By MARCELLIN P. E. BERTHELOT (*Compt. rend.*, 1899, 129, 1002—1005).—For the estimation of the elements in an organic compound, the method employed by the author for the analysis of organic compounds and determination of their heat of combustion by burning the substance in a calorimetric bomb, is recommended as being simpler and more rapid than the methods in general use. For the estimation of sulphur, phosphorus, halogens, or metals in compounds poor in carbon, it is necessary to first mix the substance with camphor or naphthalene, so as to ensure easy combustion, and in the determination of the halogens, the presence of a small amount of sodium arsenite or sulphite solution in the calorimetric bomb ensures the conversion of the whole of the halogen into the corresponding hydrogen haloid.

H. R. LE S.

Estimation of Halogens in Organic Compounds. By AMAND VALEUR (*Compt. rend.*, 1899, 129, 1265—1267).—The calorimetric bomb may be employed in the estimation of the halogens in organic compounds (Berthelot, preceding abstract). When a compound containing chlorine is burnt in compressed oxygen in the presence of ammonium hydrate, the whole of the halogen is obtained as ammonium chloride, and may be estimated by the ordinary volumetric or gravimetric methods. Bromine is estimated in a similar manner. The combustion of an organic substance containing iodine is carried out in the presence of a concentrated solution of caustic potash; the latter, which contains the whole of the halogen, is decomposed with sulphuric acid and potassium dichromate, and distilled in order to recover the iodine, which is collected in potassium iodide solution and estimated volumetrically. G. T. M.

Estimation of Benzene Vapour in Illuminating Gas. By OTTO PFEIFFER (*Chem. Centr.*, 1899, ii, 976; from *Journ. Gasbel.*, 42, 697—701).—Harbeck and Lunge's process of conversion into nitrobenzene is recommended (*Abstr.*, 1898, ii, 193). L. DE K.

Analysis of Ethereal Oils, especially the Citrus Oils. By ARTURO SOLDAINI and E. BERTÉ (*Chem. Centr.*, 1899, ii, 849—850; from *Boll. Chim. Farm.*, 38, 537—544).—These oils should conform to the following standards: *Oil of Lemon*.—Sp. gr. 0·854—0·860 at 15°. Rotatory power in 100 mm. tube +56° to +66° at 20°. Amount of citral above 6·5 per cent. On fractional distillation, the half which comes over first should show the same rotation as the original. Boiling point 171—172° under 760 mm., or 85—87° under 30—40 mm. pressure. In the absence of oil of bitter orange, the sample should not turn yellow on adding a solution of bromine in chloroform or sodium hydrogen sulphite.

Oil of Bergamot.—Sp. gr. 0·882—0·886 at 15°. Rotation at 20° +8° to +20°, generally +12° to +18°. Linanyl acetate, 34—42 per cent. Boiling point, 69° under 20—30 mm. pressure. Residue on evaporation, 5—6 per cent. Soluble in half its volume, or more, of 90 per cent. alcohol. No reaction with Schiff's test.

Oil of Bitter Orange.—Sp. gr. 0·847—0·853 at 15°. Rotation at 20°, +96° to +98°. Boiling point 173—174° under 760 mm., or 79—81° under 20—30 mm. pressure. On distillation, the rotation of the first (half) fraction is always 1° or 3° higher than the original, and it should not give a coloration with Schiff's reagent. L. DE K.

Valuation of Lemon-Oil. By J. WALTHER (*Chem. Centr.*, 1899, ii, 942—943, from *Pharm. Centr.-H.*, 40, 621—625).—The amount of citral and citronellal contained in lemon-oil is determined by converting them into oximes by means of hydroxylamine hydrochloride and then titrating the excess of this compound. A 20 per cent. solution of hydroxylamine hydrochloride in 80 per cent. alcohol is titrated first using methyl-orange and then phenolphthalein as indicator. An equal volume of the same solution is boiled with about 10 grams of lemon-oil and 0·5—1·0 gram of sodium hydrogen carbonate for 45 minutes. Hydroxylamine hydrochloride may be heated with the carbonate in presence of an indifferent liquid such as alcohol or turpentine without loss. The cooled solution is made up to 250 c.c. and 25 c.c. titrated with hydrochloric acid using methyl-orange, then back again with decinormal sodium hydroxide solution and finally again with alkali in presence of phenolphthalein. The percentages of citral c or of citronellal c' may be calculated from the formulæ $c = \frac{1·52a}{g}$ and $c' = \frac{1·54a}{g}$ in which a = c.c. of decinormal sodium hydroxide solution used, and g = weight of oil taken. By this method, lemon-oil was found to contain only 5 per cent. of citral, whereas according to Schimmel & Co., 7—8 per cent. is the usual amount. In order to avoid a large excess of hydrochloric acid, as little sodium hydrogen carbonate as possible should be used in the titration of hydroxylamine; the oximes are hydrolysed by an excess of acid,

forming ammonium citronellate and geraniate respectively, and these salts interfere with the titration.

The results were controlled by the following method. After forming the oximes, the product is made up to a certain volume, the oil separated, and the aqueous solution filtered. To 25 c.c. of the filtrate, after treating with 1 gram of sodium hydrogen carbonate, decinormal iodine solution was added, and the excess finally titrated with thio-sulphate solution. 1 c.c. of iodine solution corresponds with half a molecule of hydroxylamine

E. W. W.

Lemon Flavouring Extract and its Substitutes. By A. S. MITCHELL (*J. Amer. Chem. Soc.*, 1132—1137).—10—20 c.c. of the extract is introduced into a kind of Babcock milk bottle of 80 c.c. capacity furnished with two necks. The larger tube, used for filling should enter at the side and pass almost to the bottom of the flask. The smaller tube, used for measuring the separated oil, should have an internal diameter of about 3 mm., and a length of about 12 cm.; the tube contains 1 c.c. between its extreme graduations, and is divided to fiftieths of a c.c., each division representing 0.2 per cent. of oil when 10 c.c. of the sample have been taken.

10 drops of hydrochloric acid and 30 c.c. of water are added and the flask placed in water at 70° until the oil separates; it is then filled with warm water and whirled in the centrifuge, when the oil collects in the neck. The separation is the more complete the richer the sample is in oil, but if only 5 per cent. or less is found, an allowance of 1.2 per cent. extra should be made. The oil may now be removed with a pipette and examined in the polariscope or the Zeiss butter refractometer. The rotation of oil of lemon in a 200 mm. tube, using a Schmidt and Haensch polariscope, is 63—64°, and its refraction at 30° varies from 67—72. Lemon substitutes give widely differing figures, which are recorded in a table. The rotations of alcoholic solutions of 5 and 1 per cent. strength of oil of lemon and its substitutes are also given.

To estimate the alcohol, 25 c.c. are pipetted into a 100—110 c.c. flask; 2 c.c. each of a saturated solution of aluminium chloride and sodium hydrogen phosphate are added, the mixture diluted to 110 and well shaken. 100 c.c. of the filtrate are diluted with 25 c.c. of water and then distilled until 100 c.c. have passed over, when the sp. gr. is taken.

L. DE K.

Estimation of Mercuric Cyanide. By E. VINCENT (*J. Pharm.*, 1899, [vi], 10, 537—539).—The mercury and the nitrogen in mercuric cyanide are simultaneously estimated by heating the salt with soda-lime, the mercury being collected and weighed in the metallic state, whilst the ammonia evolved is received in standard sulphuric acid. The method, which is both rapid and accurate, is also applicable to mercuric cyanate. Commercial specimens of the latter salt are usually very impure, and largely consist of mercuric cyanide mixed with more or less oxide.

N. L.

Detection of Nitroprussides in Cases of Poisoning. By GIUSEPPE VENTUROLI (*Zeit. anal. Chem.*, 1899, 38, 743—744; from *Bull. chim. farm.*, March, 1897).—Nitroprussides are highly poison-

ous; 12 milligrams of sodium nitroprusside killed a dog when injected under the skin. Nitroprusside could not be detected in the urine, it having been completely decomposed into nitrite and thiocyanate. It is therefore recommended that a suspected liquid should be boiled with ammonium sulphide and filtered, the filtrate, mixed with potassium hydroxide, evaporated to dryness, the residue treated with absolute alcohol, and the alcoholic extract examined for nitrite and thiocyanate by the usual tests. M. J. S.

Action of Strong Aqueous Soda on Methyl Acetate in the Presence of Methyl Alcohol and Acetone. By L. CUNIASSE (*Chem. Centr.*, 1899, ii, 975; from *Ann. chim. anal. appl.*, 4, 346—347).—Methyl acetate is but imperfectly decomposed by aqueous sodium hydroxide of sp. gr. 1.3, but its solution in methyl alcohol is completely decomposed by this alkali. Acetone dissolved in methyl alcohol is insoluble in ley of the above sp. gr., and separates. If methyl acetate is present, it is then not attacked by the alkali, and is found unaltered in the layer of acetone. L. DE K.

Estimation of Fusel Oil in Alcoholic Liquids. By ERNST BECKMANN [with H. BRÜGGEMANN] (*Chem. Centr.*, 1899, ii, 731—732; from *Zeit. Unters. Nahr. Genussm.*, 2, 709—714).—The process is briefly as follows: To the spirit some dry calcium chloride is added, and the fusel oil is then extracted by repeatedly shaking with carbon tetrachloride. This extract is shaken with water to remove any ethyl alcohol, and the amyl alcohol is then converted into amyl nitrite by passing through its solution a current of dry nitrous anhydride, the flask containing it being attached to a reflux condenser. The mixture is then boiled for a short time while transmitting a current of dry carbon dioxide, and, when cold, the nitric oxide generated by bringing it in contact with ferrous sulphate is liberated and measured in a Schulze-Tiemann's apparatus, and calculated into its equivalent of amyl alcohol. The presence of ethereal compounds in commercial spirits does not interfere with the process. L. DE K.

Estimation of Geraniol in Oil of Citronella. By SCHIMMEL & Co. (*Chem. Centr.*, 1899 ii, 880; from *Geschäftsber.*, Oct., 1899).—In the ordinary method of estimating the amount of geraniol in citronella oil by forming the acetyl derivatives and hydrolysing them, geraniol and citronellal are estimated together, the latter forming isopulegol acetate. In order to estimate geraniol separately, 2 grams of the oil are warmed on the water-bath for 2 hours with 2 grams of phthalic anhydride and 2 grams of benzene. The cooled product is shaken for 10 minutes with 60 c.c. of seminormal potassium hydroxide solution, the anhydride is converted into potassium phthalate, and the acid geraniol ester into the corresponding potassium salt. The excess of alkali is titrated with seminormal sulphuric acid. By subtracting the amount of potassium hydroxide used from the amount which corresponds with the quantity of phthalic anhydride added, the alkali equivalent to the phthalic acid combined with the geraniol is obtained,

and from this the percentage of geraniol may be easily calculated. The oil of citronella was found to contain 33 per cent. E. W. W.

Wood-Tar Creosote. By LYMAN F. KEBLER (*Chem. Centr.*, 1899, ii, 827; from *Amer. J. Pharm.*, 71, 409—413).—The amount of guaiacol contained in creosote is of importance in regard to its medicinal use, and may be determined as follows: 5 c.c. of creosote are mixed with 50 c.c. of a 20 per cent. alcoholic solution of potassium hydroxide. The crystalline mass, which separates in 10—30 minutes, consists of a compound of guaiacol and creosol with potassium. The dried crystals are heated for a moment with 5 c.c. of a 10 per cent. solution of sulphuric acid, the liquid is diluted, and the mixture of guaiacol and creosol, which separates as a heavy oil, removed. By treating this oil with 4 c.c. of a concentrated solution of ammonia, the guaiacol ammonium compound is formed as a crystalline mass which separates before the less crystalline creosol compound. The latter is removed by means of benzene, and the guaiacol ammonium compound decomposed by a 10 per cent. solution of sulphuric acid. The liberated guaiacol is dissolved by shaking with benzene and finally weighed after evaporating the solvent.

The amount of creosote and phenols contained in the tar may be estimated from the diminutive of volume of the tar after extracting with an aqueous solution of glycerol. E. W. W.

Estimation of Sugar in Diabetic Urine. By GUSTAVE PATEIN and E. DUFAU (*Bull. Soc. Chim.*, 1899, [iii], 21, 1028—1033. Compare Abstr., 1899, ii, 375).—The author has repeated the experiments of Pellet, who suggests the use of normal lead acetate instead of the basic salt for the precipitation of the proteids before estimating sugar in urine, and finds that, although more accurate results are thus obtained, certain proteid substances, especially peptones, escape precipitation, both by normal and basic lead acetate, the polarimetric results being thus rendered inaccurate. If, however, the proteids are precipitated by an acid solution of mercuric nitrate, accurate and concordant results are obtained both by Fehling's solution and by the polarimeter. The existence of lævorotatory sugars in diabetic urine is exceedingly doubtful; according to Béhal's experiments, the substance which interferes with the polarimetric estimation of sugar in urine is a lævorotatory proteid, which is precipitated by heat and by nitric acid, mercuric nitrate, and alcohol, but not by acetic acid, lead acetate, or magnesium sulphate. N. L.

Rapid Estimation of Sugar in Fatty Substances. By GIOVANNI POSSETTO (*Chem. Centr.*, 1899, ii, 977; from *Giorn. Farm. Chim.*, 49, 433—435).—The sugar is extracted by treatment with a definite volume of hot water, and estimated in an aliquot part of the clear filtrate by the usual methods. L. DE K.

Rapid Process for the Estimation of Starch: Estimation of Starch in Yeast. By D. CRISPO (*Chem. Centr.*, 1899, ii, 851—852; from *Ann. chim. anal. appl.*, 4, 289—290, 290—291).—3.391 grams of the sample of starch are rubbed with water and transferred to a 200 c.c. flask; 50 c.c. of a 6 per cent. solution of potassium

hydroxide are added, the whole diluted to about 150 c.c., and heated for an hour on a boiling water-bath, with frequent shaking. When cold, the solution is diluted to the mark, filtered repeatedly, and polarised in a 200 mm. tube. If a German polariscope is used, the number of degrees of rotation multiplied by six equals the percentage of anhydrous starch.

The process may be applied to the estimation of starch in commercial yeast. The starch is first removed from the yeast by lixiviation, and finally dissolved in potash. The results are, however, somewhat below the truth. L. DE K.

Chemical Detection of Vegetable Fibres. By EDMOND JANDRIER (*J. Amer. Chem. Soc.*, 1899, 21, 1175—1176).—The sample to be examined for cotton, for instance, a piece of woollen goods, is, after careful washing, treated with sulphuric acid of sp. gr. 1.162 and heated for half an hour over the water-bath to convert the cellulose into soluble carbohydrates. The solution is diluted and a few c.c. are put into a test-tube containing about 0.01 gram of a phenol such as resorcinol. A little strong sulphuric acid is then gently poured down the side of the tube, when an orange colour will develop at the place of contact. *a*-Naphthol gives a purple, gallic acid a green gradually becoming violet, quinol and pyrogallol a brown, morphine and codeine a lavender, and thymol and menthol a pink colour. L. DE K.

Separation of Lactic, Butyric, and Valeric Acids. By SCHNEIDER (*Zeit. anal. Chem.*, 1899, 38, 775—776; from *Zeit. angew. Mikroskopie*, 1897, 45).—The mixture is distilled with superheated steam, when butyric and valeric acids pass over, whilst lactic acid remains in the residue. The distillate is evaporated to dryness with calcium carbonate, and extracted with alcohol, when calcium acetate and formate remain undissolved. From the solution, zinc nitrate precipitates zinc valerate in thin plates, and from the concentrated filtrate copper nitrate throws down copper butyrate. To identify the lactic acid, the contents of the retort are evaporated with zinc oxide and filtered while hot; zinc lactate crystallises on cooling. A few centigrams of the zinc lactate are mixed with phosphoric acid and extracted with ether. The ethereal solution is evaporated, and a little cobalt acetate and lead acetate added. A precipitate is obtained of cobalt lead lactate in the form of colourless, hexagonal plates which are feebly lævotatory. M. J. S.

Volatile Acids in Beer; Detection of Neutralising Agents in Beer. By EDUARD SPAETH (*Zeit. anal. Chem.*, 1899, 38, 745—769).—The acid reaction of normal beers is chiefly due to the presence of primary phosphates, with comparatively small quantities of volatile and non-volatile organic acids. In beer brewed with due regard to cleanliness and purity of yeast, a further development of acidity is extremely slow, and is mainly due to the production of volatile acid (acetic). In many small breweries, however, these precautions are not observed, and the conditions are often highly favourable to the access of the lactic acid bacterium. It is accordingly found that home-brewed beers, which have turned sour owe their increased acidity principally to the

development of lactic acid, whilst the amount of acetic acid is often scarcely greater than in normal beers. The proposal of Ott to recognise the fact of a sour beer having been neutralised with an alkali by estimating the volatile acids obtained by steam distillation before and after the addition of phosphoric acid, fails therefore to attain its object.

An estimation of the alkalinity of the ash of the beer will often indicate that the beer has been neutralised. The ash of 100 c.c. of normal beer rarely requires more than 0.3 c.c. of normal acid; a higher alkalinity is a qualitative indication, but for quantitative purposes the author has not been able to simplify his earlier process (*Abstr.*, 1898, ii, 407). Prior's method (*Abstr.*, 1893, ii, 53) seems also to be a trustworthy one. M. J. S.

Detection of Glycuronic Acid in Urine. By PAUL MAYER (*Chem. Centr.*, 1899, ii, 450; from *Berlin klin. Woch.*, 36, 591—593).—See this vol., ii, 155.

Determination of the Bromine Absorption of Oils. By PARKER C. McILHINEY (*J. Amer. Chem. Soc.*, 1899, 21, 1084—1089. Compare *Abstr.*, 1894, ii, 370).—The author has slightly modified his process. The oil is dissolved in carbon tetrachloride and a solution of bromine of known strength in the same solvent is added. The action of the bromine is complete in a few minutes; the bottle is placed in ice and solution of potassium iodide is introduced by the ordinary device. The excess of bromine liberates iodine, which is then titrated with *N*/10 solution of sodium thiosulphate.

If rosin or rosin oil is present, hydrogen bromide will be also formed; this is estimated by adding to the bleached liquid a solution of potassium iodate. This, in the presence of potassium iodide and the acid, liberates iodine, which is then again titrated and calculated into hydrogen bromide. L. DE K.

Detection of Sesamé Oil. By A. BÖMER [with K. WINTER] (*Chem. Centr.*, 1899, ii, 729—730; from *Zeit. Unters. Nahr.-Genussm.*, 2, 705—709).—The author has investigated the properties of sesamin, one of the unsaponifiable constituents of sesamé oil, in which it occurs to the extent of 0.2—0.5 per cent. It is very soluble in chloroform but only slightly so in ether or light petroleum; by means of ether, it may be readily separated from phytosterol. The unsaponifiable portion of sesamé oil is first crystallised from alcohol and the crystals are then washed with small quantities of ether until the undissolved mass is free from phytosterol crystals. Sesamin is colourless, crystallises in large needles, or forms irregularly shaped, round crystals, and melts at 120—122°; when contaminated with phytosterol, the melting point may be as low as 110—112°. A mixture of equal parts of acetic anhydride and sulphuric acid added to sesamin causes a brownish-green, then bluish-green, finally dark cherry-red, or reddish-blue coloration. Sulphuric acid added to the chloroform solution turns cherry-red or blue, leaving the chloroform colourless; water does not discharge the colour. Its alcoholic solution turns violet on adding

sulphuric acid. Solutions of sesamin show a right-handed polarisation. It seems incapable of esterification.

Sesamé oil contains a small quantity of an active principle to which the Baudouin reaction, so characteristic of this oil, is due. This substance may be removed from the mother liquor of the crude phyto-sterol or even from sesamé oil itself by treatment with animal charcoal. From the charcoal, it may be recovered by treatment with ether; it then forms a pure brown or reddish-brown, resinous mass which still gives the Baudouin reaction in a dilution of 1:500,000. As this substance is affected by heat, care must be taken to avoid over-heating when testing margarine for sesamé oil.

L. DE K.

Milk Analyses: New Process for the Simultaneous Estimation of Residue, Fat, and Ash. By H. TIMPE (*Chem. Centr.*, 1899, ii, 977; from *Zeit. öffentl. Chem.*, 5, 413—416).—5 c.c. of milk are introduced into a weighed Gooch's crucible filled with asbestos and the residue is obtained by drying for 4—5 hours in an air-bath at 100—102°.

The fat is extracted with ether, the crucible being placed in a Soxhlet's apparatus, and the ash found by incineration.

L. DE K.

Determination of the Melting Point of Fats. By FERDINAND JEAN (*Chem. Centr.*, 1899, ii, 973; from *Ann. chim. anal. appl.*, 4, 331—334).—A platinum wire, such as is used for making borax beads, is dipped into the liquid fat and the bead allowed to cool for 4 hours. It is then attached to the bulb of a thermometer and suspended in a beaker containing water; heat is applied and the temperature is noticed first when the edges of the fat become translucent and then when the whole globule is transparent, the mean of the two observations being taken as the melting point. If the fat does not melt to a clear liquid, the wire is first bent like an 8, dipped into the fat, and when cold it is pulled straight. The temperature at which the fat detaches itself from the wire and floats on the water is taken as the melting point.

L. DE K.

Detection of Acetaldehyde in Ether. By HERMANN BLASER (*Chem. Centr.*, 1899, ii, 848; from *Pharm. Centr.-Halle*, 40, 607).—Instead of using a solution of magenta decolorised with sulphurous acid, the author takes a very weak solution of magenta (1:100,000) and bleaches this completely by exposure to sunlight. This solution gives very sharp reactions with aldehyde.

L. DE K.

[Detection of] **Acraldehyde and certain other Aldehydes.** By LOUIS LEWIN (*Ber.*, 1899, 32, 3388—3389).—Acraldehyde gives a gentian-blue coloration with a mixture of piperidine and a solution of sodium nitroprusside; very dilute solutions give a greenish-blue colour, but the reaction can be observed at a dilution of 1:3000; the blue colour becomes violet on adding ammonia, rose-violet to rusty-brown with sodium hydroxide, and brown with mineral acids, the blue colour returning on adding water. Dimethylamine can be used in place of piperidine, but is much less sensitive.

Acetaldehyde gives a similar blue coloration even at a dilution of 1:10,000, paraldehyde and propaldehyde at 1:1000, and cinnamaldehyde in alcohol solution a green to blue colour. Formaldehyde, trichloroaldehyde, isobutaldehyde, benzaldehyde, salicylaldehyde, phenylacetaldehyde, cenanthaldehyde and furfuraldehyde give no coloration with this reagent. T. M. L.

Detection of Acetone in Urine and other Animal Secretions. By CARL OPPENHEIMER (*Chem. Centr.*, 1899, ii, 888—889; from *Berl. klin. Woch.*, 36, 38).—Denigé's process (*Abstr.*, 1899, i, 22; ii, 256) with mercuric sulphate containing excess of sulphuric acid is recommended. When applying the process quantitatively, the factor 0.055 should be substituted for 0.06 when calculating the weight of the mercurial acetone compound to acetone. L. DE K.

New Methods in Indigo Assay. By ROBERT CLAUSER (*Chem. Centr.*, 1899, ii, 978—979; from *Oesterr. Chem. Zeit.*, 2, 521—523).—After pointing out the defects of the present methods, the author states that the best results are obtained by means of a slight modification of Schneider's naphthalene process.

0.3—0.5 gram of the powdered sample is mixed with quartz sand and extracted by means of 30—40 grams of boiling naphthalene. The naphthalene cake, which contains all the indigo, is then extracted in a specially constructed apparatus with 200 c.c. of boiling ether, and the indigo which is left undissolved is collected on asbestos and weighed. L. DE K.

A New Alkaloidal Reagent. Detection of Opium. By MECKE (*Chem. Centr.*, 1899, ii, 683—686; from *Zeit. öffentl. Chem.*, 5, 351—354).—The reagent is made by dissolving 0.5 gram of selenous acid in 100 grams of sulphuric acid. A complete table and a lengthy description are given showing the action of the acid on the alkaloids in the cold and on warming.

By means of the intense bluish-green coloration given by the new reagent, it is possible to detect with certainty the presence of the rarer opium alkaloids in suspected cases of poisoning with that drug. L. DE K.

General and Physical Chemistry.

Method for the Exhibition of the Properties of Polarised Light. By NICOLAI A. UMOFF (*Zeit. physikal. Chem.*, 1899, **30**, 711—715).—The paper contains an account of a number of interesting lecture experiments. If a beam of plane polarised light is projected on to a glass cone with a vertical angle of about 68° , to the base of which is attached a paper screen, a circular disc of light is formed on the screen, by reflection from the glass, with two dark minima 180° apart, these showing the plane of polarisation. Various colour effects are obtainable by interposing plates of quartz, &c. By downward reflection of the beam into a glass jar of water, to which has been added a little alcoholic solution of resin, two dark lines down the opalescent liquid mark the plane of polarisation and one of the most interesting suggestions is the replacing of the water by a solution of sugar, &c., when spiral dark bands are obtained, illustrating the rotation of the plane of polarisation. L. M. J.

Spectrum of Silicon. By SIR NORMAN LOCKYER (*Proc. Roy. Soc.*, 1899, **65**, 449—452).—A double line previously found in the spectra of gases distilled from the mineral eliasite was probably due to the fusion of the glass, and in reality belongs to silicon, of which element several other lines have now been detected. The silicon lines may be divided into three sets, no two of which behave alike under varying electrical conditions. It is found that the three sets of lines respectively attain a maximum intensity at the levels of stellar temperature represented by β , γ , and ζ Orionis. A line, however, at λ 3905.8, occurring in both arc and spark spectra, is not represented in the spectra of any of these stars. J. C. P.

New Lines in the Ultra-red of the Argon Spectrum. By RAFFAELE NASINI, FRANCESCO ANDERLINI, and ROBERTO SALVADORI (*Real. Accad. Lincei*, 1899, [v], **8**, ii, 269—271).—By photographing the ultra-red portion of the spectra of various natural gases, including gas from a fumarole on Vesuvius and that of the Grotta del Cane, new argon lines of the following wave-lengths are detected: 798.0, 803.0, 814.0, 832.0, 845.0, and 857.5. T. H. P.

Reversible Photochemical Processes. By ROBERT LUTHER (*Zeit. physikal. Chem.*, 1899, **30**, 628—680).—The changes investigated were the blackening of silver chloride and silver bromide; this being attended with the liberation of halogen, it is probable that for any particular light intensity the products are in equilibrium when the pressure of the halogen reaches a certain value. In order to determine the relation between the light intensity and the halogen pressure, observations were made of the intensity necessary to cause blackening of glass plates coated with deposits of silver chloride and bromide, the deposits being in contact with halogen solutions of

varying strength, details of the method adopted being given. Curves are obtained for log. concentration against log. light intensity. The question is also investigated theoretically, and the author deduces an equation for the variation of the equilibrium constant with illumination, namely, $RT\{\log K_{\text{bright}} - \log K_{\text{dark}}\} = C/3 \sum a_x v_x (l_x - 1)$, where C represents the concentration of the light rays, and a_x , v_x and l_x are the molecular coefficients, molecular volume, and the capacity function for radiations of the several substances entering into the reaction. Hence the equilibrium constant is unaffected by light only when this expression is zero; in general, the form is $\log K = AI + C$, where I is the light intensity and A and C are constants, but the experimental results are not in accord with these deductions. The E.M.F.'s of platinum electrodes in various illuminated halogen solutions, that is, the oxidation potentials of the solutions, were also determined, and the comparison of these values with the light intensity again shows no accord with the theories of either the author or of Luggin. No evidence could be obtained of a reverse process, that is, no light phenomena are obtainable by the chlorination of the darkened products. The values 1.44 and 1.14 volts were obtained for the E.M.F.'s of respectively bright and dark silver chloride electrodes in $N/10$ chloride solution. By determinations of the E.M.F. of a platinum electrode in a solution containing silver powder with varying quantities of chlorine or bromine, evidence was obtained of the existence of the compounds Ag_2Cl and Ag_2Br , but no other compounds are indicated. Further work on the same question is promised by the author.

L. M. J.

Absorption of Röntgen's Rays by Aqueous Solutions of Metallic Salts. By LORD BLYTHSWOOD and E. W. MARCHANT (*Proc. Roy. Soc.*, 1899, 65, 413—428).—The absorption of normal solutions of salts with the same acid radicle increases with the atomic weight of the metal, although the increase in some cases, for example, calcium, strontium, and barium, is not very marked. Bromides and iodides are all highly absorbent, and of other salts nitrates, chlorides, and sulphates are placed in the order of increasing absorptive power. The absorption in a given thickness of salt solution is not proportional to the concentration, but follows approximately a logarithmic law. The amount of absorption varies logarithmically with the thickness of the solution traversed by the rays. The results are largely confirmatory of those obtained by Gladstone and Hibbert (*Abstr.*, 1897, ii, 131; *Chem. News*, 1898, 78, 199).

J. C. P.

Radiations from Radium. By HENRI BECQUEREL (*Compt. rend.*, 1900, 130, 206—211. Compare this vol., ii, 81, 125, 126).—The rays emitted by the chloride and carbonate of radium are equally deviated by the electro-magnet, the radiation from different specimens varying in intensity, but not in kind. The deviation produced by a given magnetic field remains constant, whether the experiments are made in air or in a vacuum. The remainder of the paper contains an account of physical experiments not suitable for abstraction.

G. T. M.

Dispersion of the Radiation of Radium in a Magnetic Field. By HENRI BECQUEREL (*Compt. rend.*, 1900, 130, 372—376. Compare this vol., ii, 126).—The author continues his researches on this subject, and describes various experimental improvements which enable him to obtain more definite results. N. L.

Electromotive Force and Chemical Equilibrium. By VICTOR ROTHMUND (*Zeit. physikal. Chem.*, 1899, 31, 69—78).—When k is the equilibrium constant of a chemical process which in a galvanic element originates the electromotive force E , then $E = RT \log_e k$: application of this general equation to the system:—metal | oxide | KOH | oxygen at atmospheric pressure | platinum, leads to the equation

$$\Pi = (L_m/c_m)^{4/n} \cdot (L_0/c_0)^4,$$

where Π is the dissociation pressure of the metallic oxide, n the valency of the metal, L_m and L_0 the electrolytic solution pressures of the metal and oxygen, c_m and c_0 the concentrations of the metal and hydroxyl ions respectively. When the solution is saturated with oxide, the product $c_m^{1/n} \cdot c_0 = \text{a const.}$, so that the dissociation pressure of an oxide depends, not only on the electrolytic solution pressure of the metal, but also on a constant peculiar to the oxide. In general, however, the order of affinity of metals for oxygen will be determined by their electrolytic solution pressures.

The E.M.F. of the combination Pt | O₂ | NaOH | HgO | Hg is 0.159 volt; from this value, with the equation $E = RT \log_e \Pi$, the dissociation pressure Π of mercuric oxide is calculated to be $10^{-8.08}$ mm. of mercury at ordinary temperatures; this does not agree with the value calculated from Pélabon's numbers (*Abstr.*, 1899, ii, 423) and the heat of formation of mercuric oxide.

A theoretical connection is established between the dissociation constant of a gas and the electrolytic solution pressures of its components; thus it is shown that the dissociation of hydrogen iodide can be calculated from the electrolytic dissociation of aqueous hydriodic acid, Henry's partition coefficients, and the electrolytic solution pressures of hydrogen and iodine. The author urges investigation of the relation between various equilibrium constants, and advocates the use of ergo-chemical equations. J. C. P.

A New Kind of Transition Element. By ERNST COHEN (*Proc. K. Akad. Wetensch. Amsterdam*, 1899, 2, 153—158; *Zeit. physikal. Chem.*, 1899, 30, 623—627).—Although below 20° the grey modification of tin is the stable one, yet the white modification may be supercooled, and an element may accordingly be constructed of the form:—Electrode of grey tin | Solution of a tin salt | Electrode of white tin. The E.M.F. will be $0.0001983 \frac{T}{n} \log_{10} P_g/P_w$ volt for this element where n is the valency of the tin, P_g and P_w the electrolytic solution pressures of the grey and white modifications respectively. Actual measurement of the E.M.F. showed that the ratio P_w/P_g was 1 at 20°, the transition temperature, and >1 at temperatures below 20°. Thus the white modification has the greater electrolytic solution pressure, and will precipitate grey tin from solutions of tin salts below 20°, a conclusion confirmed by experiment. This explains why a

solution of a tin salt is highly favourable to the conversion of the white into the grey modification.

When E_1 is the difference of potential between the grey tin and the tin solution in which it is immersed, i_1 the heat of ionisation of the grey tin, and $e_0 = 96540$ coulombs, then $E_1 = i_1/ne_0 + T.dE_1/dT$: a corresponding relation holds for the other electrode. Combining these with the equation $T.dD/dT = r_1/(V_w - V_g)$, where D is the external pressure, r_1 the heat evolved when 1 kilogram of white tin is converted into grey tin, V_w and V_g the volume in cubic metres occupied by 1 kilogram of the white and grey modifications, the author deduces the equation $dT/dD = 0.00105 A(V_w - V_g)/n(dE_1/dT - dE_2/dT)$, A being the atomic weight of the metal forming the electrode. J. C. P.

Theory of the Transition Cell of the Third Kind. By ERNST COHEN (*Proc. K. Akad. Wetensch. Amsterdam*, 1899, 2, 334—342. Compare Abstr., 1898, ii, 276).—The general type of this transition element consists of two cells coupled in opposition—(a) electrode reversible with respect to the anion | saturated solution of a salt S in contact with the stable solid phase of the salt | electrode reversible with respect to the cation, and, (b) electrode reversible with respect to the anion | saturated solution of the salt S in contact with the metastable solid phase of the salt | electrode reversible with respect to the cation; S, for example, may be zinc sulphate, the transition temperature of the hydrates $ZnSO_4 \cdot 7H_2O$ and $ZnSO_4 \cdot 6H_2O$ being 39° . The temperature coefficient of this transition element at 39° is calculated in the following way. Differentiation of the equation $E = q(P - T)/P$, leads to $dE/dT = -q/P$, where E is the E.M.F. of the element, q the heat effect of the change involved, and P the absolute transition temperature of the change; q is calculated by extrapolation from Thomsen's figures, and also determined experimentally, leading to dE/dT at $39^\circ = -0.51$ millivolts. From Jaeger's values (compare Abstr., 1898, ii, 202) for the E.M.F. of Clark cells containing solid $ZnSO_4 \cdot 7H_2O$ or $ZnSO_4 \cdot 6H_2O$, it may be shown that dE/dT at $39^\circ = -0.55$ millivolts, agreeing well with the calculated coefficient.

The solubilities of both hydrates of zinc sulphate have been determined at temperatures between -5° and 39° , and results obtained agreeing closely with those of Callendar and Barnes (Abstr., 1898, ii, 276). J. C. P.

Alleged Identity of Red and Yellow Mercuric Oxides. I. By ERNST COHEN (*Proc. K. Akad. Wetensch. Amsterdam*, 1899, 2, 273—281).—The E.M.F. of the system mercury | red mercuric oxide in caustic potash | yellow mercuric oxide in caustic potash | mercury has been very carefully determined by comparison with a standard cell at 25° . To begin with, the E.M.F. was 0.585 millivolt, but it increased to a maximum of 1.237 millivolts in about 24 hours, falling thereafter, and reaching a constant value, 0.685 millivolt, after 170 hours. When the oxides were previously shaken with water to remove soluble matter, and left in contact with the aqueous caustic potash before being put in the cell, the E.M.F. was constant from the first, and equal to 0.685 millivolt. It thus appears that red and yellow mercuric oxides are isomeric, contrary to Ostwald's view (*Zeit. physikal.*

Chem., 1895, 18, 159). The author's results are also at variance with those of Glazebrook and Skinner, according to whom a difference of 7 millivolt exists at 12° between the E.M.F. of Gouy standard cells made with the two oxides (*Phil. Trans.*, 1892, 183, 367). J. C. P.

Metallic Crystallisation by Electrical Transport of Certain Metals in Distilled Water. By THOMAS TOMMASINA (*Compt. rend.*, 1900, 130, 325—327).—When an electric current of less than 1 milli-ampère is sent through flat zinc electrodes placed in distilled water, the electrodes being very close to each other, well defined crystals of metallic zinc are deposited. At first, no gas is evolved, but after the action has been going on for some time, there is an evolution of gas from the cathode, the electrodes become oxidised, and the deposition of the metal ceases. If the anode is removed, cleaned, and then replaced, the action begins again. With a copper plate as cathode, and a zinc anode, crystals of zinc are deposited on the copper. Similar results were obtained with silver and cadmium. If the two electrodes are too widely separated, then a kind of haze appears between them; this contains very small, metallic crystals, which are arranged in a chain-like form. H. R. LE S.

Polarisation Phenomena observed in Quantitative Electrolytic Determinations. By HUGH MARSHALL (*Proc. Roy. Soc. Edin.*, 1899, 22, 532—538).—Attempts have been made to determine the time necessary for the complete electrolytic deposition of nickel, with varying current strengths, and different quantities of metal. With a cathode current density of 0.6—0.7 ampère per sq. decim., the time required for the deposition of 0.1—0.5 gram nickel was found to be 4 hours; the volume of the solution was 135 c.c., and it contained 5 grams each of ammonium sulphate and ammonia. In certain cases, the voltmeter showed a rise of 0.5 volt towards the end of the operation, and precisely in these cases was the deposition of the nickel complete. This rise of potential may, in fact, be taken as an indication that all the nickel has been deposited, as is shown by a number of test experiments.

The removal of the last traces of nickel from the solution is thus accompanied by an increased resistance between the electrodes. Experiment shows that, when the potential begins to rise, only 2—3 mg. of nickel remain in solution. When small quantities of nickel have to be estimated, it is advisable to use a small volume of solution and a small vessel, in which case the rise of potential above referred to is more marked and rapid. It remains to be seen whether this polarisation effect, probably due to a film on the cathode, can be trusted to appear in all cases. J. C. P.

Electrolytic Reduction of Potassium Chlorate. By ADOLPH L. VOEGE (*J. Physical Chem.*, 1899, 3, 577—601).—The investigations were made with the object of collecting data to serve as basis for a theory of electrolytic reduction. Electrolysis in acid and alkaline solutions showed that the percentage quantity of hydrogen used in the reduction is greater in the former than in the latter, and is, moreover, a function of the current, decreasing with increasing current density.

In the further experimental work, solutions in dilute sulphuric acid were chiefly used. The reduction varies with the metal employed as electrode, and was greater for zinc than for platinum, being also dependent on the physical structure; in the case of cadmium, the reduction efficiency did not alter with varying current density, so that this metal is less efficient than zinc for weak currents, but more efficient for strong currents. The effect of the acid concentration was determined, and it was found that the maximum efficiency was obtained for acid about $3/4$ normal, the potassium chlorate being about $1/2$ concentrated at 64° . Rise of temperature causes an increase of efficiency, the reduction being increased from 52 to 90 per cent. by a rise of from 25.6° to 81.1° . Potassium chloride was usually found in the anode liquid, but this was due entirely to diffusion from the cathode liquid, and not to any anodic reduction. A greater reduction than that due to the electrolytic hydrogen is sometimes obtained, this being most probably caused by the secondary action of the zinc on the potassium hydroxide, produced at the cathode, with the consequent formation of potassium zinc-oxide and hydrogen. Copper was found to readily dissolve in the acid solution of potassium chlorate, with no evolution of hydrogen, but with a 98 per cent. yield of potassium chloride; the *electrolytic* reduction with copper electrodes, however, is not as great as in the case of zinc electrodes.

L. M. J.

The Dilution Law. By WILDER D. BANCROFT (*Zeit. physikal. Chem.*, 1899, 31, 188—196).—The empirical formula $K = C_i^n / C_s$ is suggested as a general expression of the dilution law, where C_i and C_s are the volume concentrations of the dissociated and undissociated portions respectively; K and n vary for different electrolytes. By using Kohlrausch's numbers for ten strongly dissociated salts, and plotting $\frac{1}{2} \log C_i$ along one axis, and $\frac{1}{2} \log C_s$ along the other, the author shows that the curve obtained for each electrolyte is a straight line, and that n may be calculated in each case from the pitch of the curve; K may then be calculated for each dilution, and from the mean of the values so found the degree of dissociation which satisfies the equation $K = C_i^n / C_s$ may be calculated and compared with the observed value. A remarkably good agreement is obtained, except in the case of the most concentrated solutions; n varies from 1.36 for potassium chloride to 1.55 for silver nitrate. It is suggested that the generalised dilution law may give more accurate values for the dissociation in concentrated solutions than can be obtained from conductivity determinations.

J. C. P.

Molecular Susceptibility of the Salts of the Rare Earths. By STEFAN MEYER (*Ber.*, 1900, 33, 320—321. Compare du Bois and Liebknecht, this vol., ii, 127).—The author's values for the molecular magnetism of the series praseodymium, neodymium, samarium, gadolinium, and erbium, derived from a study of their dry compounds, indicates that their susceptibility coefficients have the following relative values: Pr : Nd : Sm : Gd : Er = 2 : 5 : 10 : 23 : 40, whilst from the data furnished by du Bois and Liebknecht from their determinations of the atomic magnetism in solutions of the salts of the rare earths, the following ratio is obtained: Pr : Nd : Sm : Gd : Er =

3:5:12:26:37. The discrepancy in the two series is probably due to the variable quantities of impurities present in the substances under examination, the paramagnetism of yttrium and ytterbium, for example, being almost certainly due to the presence of other elements.
G. T. M.

Molecular Susceptibility of the Paramagnetic Salts of the Iron Group. By OTTO LIEBKNECHT and A. P. WILLS (*Ber.*, 1900, 33, 443—445. Compare this vol., ii, 127).—Determinations of the magnetic susceptibility of 36 salts of the metals chromium, manganese, iron, cobalt, nickel, and copper have been made, and the results are indicated in tabular form. The salts of cobalt are placed next to those of iron on account of the close relationship existing between the magnetic properties of these elements, whether free or combined. When the series is arranged in this order, the molecular susceptibility attains its maximum at iron and manganese and falls to its minimum at copper. The susceptibility of the complete series of halogen salts was determined in the case of bivalent manganese, cobalt, and nickel; it was found to increase from the fluoride to the chloride and then fall to a minimum value for the iodide.
G. T. M.

Electrolytic Dissociation of Certain Salts in Methyl and Ethyl Alcohols, as Measured by the Boiling Point Method. By HARRY C. JONES (*Zeit. physikal. Chem.*, 1899, 31, 114—141).—In the various forms of boiling point apparatus, there are two defects: (1) too little attention is paid to the effect of radiation, (2) the condensed solvent is returned directly into the boiling liquid. An apparatus, resembling in some respects that of Hite (*Abstr.*, 1895, ii, 479), has been devised and used by the author, in which a cylinder of platinum foil is placed between the thermometer and the walls of the boiling tube; this reduces the effect of radiation, and prevents the condensed solvent coming in contact with the thermometer before it is reheated. The boiling tube is surrounded by an asbestos jacket, and rests on a piece of wire gauze, which is directly heated by the flame.

With this comparatively simple apparatus, the author has studied the effect of various dissolved substances on the boiling points of methyl and ethyl alcohols. Determinations with acetanilide, acetamide, diphenylamine, and triphenylmethane gave a mean value of 8.4 for the boiling point constant of methyl alcohol. Experiments then made with dissociating inorganic compounds allowed the degree of dissociation to be determined. The bromides and iodides of potassium and ammonium are dissociated to the extent of about 50 per cent., whilst the dissociation of sodium bromide and iodide is greater. Potassium and sodium acetates are dissociated to about 37 per cent., calcium nitrate to about 14 per cent. Most of the solutions contained 1/100th—1/50th of the molecular weight per 100 grams of solvent.

Generally, similar results were obtained with ethyl alcohol as solvent. The following degrees of dissociation were determined: potassium iodide 25—27 per cent., sodium iodide 31—33 per cent., sodium bromide 26—27 per cent., ammonium bromide 20—21 per

cent., sodium and potassium acetates 13—15 per cent., calcium nitrate 4—5 per cent.

Comparison of the dissociation of various inorganic compounds in water, methyl alcohol, and ethyl alcohol leads to the conclusion that there is not a proportionality between the dielectric constants of these solvents and their dissociating power, although the dielectric property seems to be the chief factor concerned. Other solvents with high dielectric constants, such as formic acid, allyl alcohol, acetone, nitrobenzene, *o*-nitrotoluene, will have to be investigated in order to settle the point satisfactorily.

J. C. P.

Specific Heats of some Organic Substances. By GUSTAVE FLEURY (*Compt. rend.*, 1900, 130, 437).—The specific heats of some dry clothing materials were determined, with the following results: cellulose, 0.366; wool, 0.393; leather, 0.357. In the ordinary moist state, these substances contain 7, 11, and 16 per cent. of water respectively, and the specific heats are: cellulose, 0.41; wool, 0.459; leather, 0.45.

N. L.

Atomic Weights and Physical Properties. By THOMAS BAYLEY (*Chem. News*, 1899, 80, 282).—The product of melting point (absolute) and coefficient of linear expansion has a nearly constant value 0.02 for certain elements. The value of x in the equation (specific heat) \times (melting point) = x (atomic weight) is given for a number of elements.

J. C. P.

Change in the Transition Point of Ammonium Nitrate at 32° through addition of Potassium Nitrate. By WOLF MÜLLER (*Zeit. physikal. Chem.*, 1899, 31, 354—359).—If t_0 and t_1 are the transition temperatures of ammonium nitrate before and after addition of potassium nitrate, and c is the molecular concentration of potassium nitrate in 100 grams of ammonium nitrate, the molecular depression of the transition point is $(t_0 - t_1)/c$; this molecular depression diminishes as the concentration of potassium nitrate increases, and the change takes place according to Rothmund's equation $t_0 - t_1 = RT^2/q \cdot (c_2 - c_1)$, where T is the absolute transition temperature of pure ammonium nitrate, c_2 and c_1 the molecular concentrations of potassium nitrate in 100 grams of the two modifications of ammonium nitrate, and q the heat of transition (compare Abstr., 1898, ii, 158). The results obtained seem to show that the transition of ammonium nitrate at 32° consists in a change of quadruple into triple molecules.

J. C. P.

New Method of Determining Transition Temperatures. By ERNST COHEN (*Zeit. physikal. Chem.*, 1899, 31, 164—175).—Systems which pass into each other are equally soluble at their transition temperatures. By measuring at various temperatures the electrical resistance of saturated solutions of the stable and metastable modifications, two curves are obtained connecting temperature and resistance, and these curves cut each other at the temperature of transition. An apparatus is described in which the preparation of the saturated solution and the measurement of the resistance can be conveniently made. The application of the method to the systems $\text{ZnSO}_4 + 7\text{H}_2\text{O}$ and $\text{ZnSO} + 6\text{H}_2\text{O}$ gave for the transition temperature 39°, in agreement with the values obtained by other methods (Abstr., 1898, ii, 276;

this vol., ii, 184). The metastable form below 39° , $\text{ZnSO}_4 + 6\text{H}_2\text{O}$, is obtained by covering a solution saturated about 60° with a layer of paraffin oil, and allowing it to cool very slowly in a large water-bath.

The method is also employed for determining the resistance of a saturated copper sulphate solution at various temperatures; the curve connecting temperature and resistance shows in this case a slight discontinuity at 56° . A Daniell cell, in which a saturated copper sulphate solution is combined with a 5 per cent. zinc sulphate solution, shows a discontinuity in the E.M.F. curve at the same temperature. The author criticises Preece's (*Proc. Roy. Soc.*, 1883, 35, 48) and Carhart's experiments on the internal resistance of the Daniell cell.

J. C. P.

Partial Association of Liquid Molecules. By J. J. VAN LAAR (*Zeit. physikal. Chem.*, 1899, 31, 1—16).—A thermodynamical treatment of the subject with a number of involved calculations. The equation $(\text{H}_2\text{O})_2 \rightleftharpoons 2\text{H}_2\text{O}$ represents the equilibrium between the simple and double water molecules, and the association is accompanied by the absorption of 1930 cal. per 18 grams at 0 — 60° . For ethyl alcohol, a similar equation holds, whilst methyl alcohol and acetic acid are to be regarded as consisting partly of triple molecules.

The change of 18 grams of simple water molecules into double molecules is accompanied by an expansion of 8.44 c.c., the corresponding expansion for 46 grams of ethyl alcohol being 2 c.c.; the contraction which occurs in mixing water and ethyl alcohol therefore points to a decrease in the number of associated molecules. It is further shown that the partial association of the molecules explains the irregular thermal expansion of water.

J. C. P.

[Negative Heat of Formation of Alloys of Zinc and Copper]. By ALEXANDER GALT (*Proc. Roy. Soc. Edin.*, 1899, 22, 137—149 and 619—621).—By determining the heat of solution in dilute nitric acid of a powdered alloy and of a mixture of the two component metals in the same proportion, the heat of formation of the alloy may be ascertained. Copper-silver alloys shows little or no heat of formation. Copper-zinc alloys containing more than 30 per cent. of copper have a considerable positive heat of formation, but if the percentage of copper is less than 30, the heat of formation is negative.

J. C. P.

[Thermochemistry of] the Uric Acid Series. By MARCELLIN P. E. BERTHELOT (*Compt. rend.*, 1900, 130, 366—372).—The following determinations were made with the object of ascertaining the thermal effect of oxidation and methylation in the uric acid series.

Substance.	Heat of combustion.		Heat of formation.
	At constant volume.	At constant pressure.	
1-Methylpurine	820.88 Cal.	820.60 Cal.	- 47.74 Cal.
7-Oxypurine	583.57 "	582.69 "	+ 26.86 "
2-Oxypurine	592.47 "	591.59 "	+ 17.96 "
1-Methyl-7-oxypurine	760.08 "	759.49 "	+ 13.37 "

A comparison of these figures with the results previously obtained for xanthine (Abstr., 1899, ii, 400) shows that the conversion of 7-oxypurine (hypoxanthine) into xanthine and uric acid by the successive fixation of oxygen develops 69·8 Cal. and 51·4 Cal. respectively; from the former figure, the heat of formation of purine itself is calculated as -44 Cal. The decreasing development of heat for successive additions of oxygen is in accord with the results obtained in the indole series (*loc. cit.*). The conversion of hypoxanthine into 1-methylhypoxanthine is accompanied by the absorption of 13·5 Cal., instead of by the development of 5—6 Cal. as is commonly the case with homologous compounds; the difference between the heats of combustion (176·8 Cal.) is also greater than the normal (157 Cal.). Methylation is therefore accompanied by an increase in the energy of the system, just as is the case with the three methylxanthines, and Matignon's observations as to the anomaly exhibited by compounds in which the methyl group is directly united to nitrogen are confirmed. By deducting from the heat of formation of methylpurine the difference between the corresponding figures for hypoxanthine and methylhypoxanthine, the heat of formation of purine is found to be -34·2 Cal. as against the value -44 Cal. deduced above from the oxidation phenomena.

N. L.

Heat of Dissociation of Violuric Acid and of Water. By RICHARD ABEGG (*Ber.*, 1900, 33, 393—394).—Guinchard has shown (Abstr., 1899, i, 781) that the dissociation constant of violuric acid increases rapidly as the temperature rises; from his values, the heat of dissociation can be calculated by van't Hoff's formula, the mean value being about -3700 Cal. This is about 10 times as great as the values obtained with acetic and other weak acids, and confirms the view that the ionisation is accompanied by an (endothermic) isomeric change.

In a similar way, the high value of the heat of dissociation of hydrogen fluoride (-3550 Cal.), when compared with hydrogen chloride (-1080 Cal.) and hydrogen bromide (-1617 Cal.), is an indication that the ionisation is accompanied by the dissociation of H_2F_2 into 2HF .

The heat of dissociation of water into the ions H^+ and OH^- is very large, amounting to -13000 Cal., and this is regarded as due in part to its high association factor, the complex molecules $(\text{H}_2\text{O})_x$ being broken down into $x\text{H}_2\text{O}$ in the ionisation.

T. M. L.

Antimony Trichloride in Cryoscopy. By STANISLAW TOLLOCZKO (*Zeit. physikal. Chem.*, 1899, 30, 705—710).—According to the views of Brühl (Abstr., 1899, ii, 10), the dissociating power is due to incomplete saturation of the solvent, and if so, marked dissociation should be found for solutions in antimony trichloride, a compound which, owing also to its convenient freezing point, is well adapted for cryoscopy. The cryoscopic constant was found to be 184 by determinations of the depressions produced by xylene, anthracene, diphenylmethane, acetophenone, and benzophenone; this high constant, ten times that of water, indicates a latent heat of fusion of 12·9 cal. With potassium chloride and potassium bromide, indications of consider-

able dissociation were obtained, increasing with dilution, the value 0.69 being obtained for the bromide at a concentration of about 0.2 per cent. Brühl's views have hence, in this case, been confirmed (see, however, Kahlenberg and Lincoln, *Abstr.*, 1899, ii, 397). The author points out the suitability of the substance as a solvent for cryoscopic determinations of the molecular weight of organic compounds; which are for the most part soluble in it. L. M. J.

Real and Apparent Freezing Points and Cryoscopic Methods. By MEYER WILDERMANN (*Zeit. physikal. Chem.*, 1899, 30, 577—585. Compare *Abstr.*, 1896, ii, 290).—The paper, much of which has been previously published, is essentially a recapitulation of the errors inherent in freezing point determinations. Even if the instruments are absolutely accurate, and if no accidental extraneous errors exist, the freezing point observed is not the true freezing point, but a temperature dependent on the velocity of precipitation or of melting of the ice, the rate of cooling, and the variation from the convergence temperature. Identity of results obtained under similar conditions is thus no indication that these yield the true temperatures desired, so that repetition of experiments leads to no final accuracy. As the errors are functions of the temperature, the observed depressions are also inaccurate, and it is only by determining the magnitude of each effect, and correcting for it, that really trustworthy determinations of freezing points and cryoscopic depressions can be obtained. Examples are given where neglect of this may lead to errors of 6 to 12 per cent. The same reasoning applies also to determinations of boiling points and other constants, but these are not further considered (compare this vol., ii, 131).

L. M. J.

Thermokinetic Properties of Solutions. By LADISLAUS NATANSON (*Zeit. physikal. Chem.*, 1899, 30, 681—704).—A purely mathematical paper, in which the author discusses, from a thermodynamical standpoint, a system consisting of a mixture separated from a pure substance, but in which the passage of one component in either direction is permitted. When the pure substance is one component of the mixture, the case reduces to one of a solvent separated from a solution by a semipermeable partition, and two values are deducible for the osmotic pressure, according to the component which is regarded as the solvent. In a solution, therefore, there are two osmotic pressures and it should not be impossible in certain cases, as for two miscible liquids, to experimentally verify this. L. M. J.

Liquefaction of Gaseous Mixtures. By F. CAUBET (*Compt. rend.*, 130, 167—169).—Curves representing the tension of saturated vapour against temperature are given for methyl chloride, carbon dioxide, and ten different mixtures of these compounds, the determinations being carried to the critical temperature; the tangent to each curve at its critical point forms the critical line for these mixtures. Retrograde condensation is observed under those conditions represented by the portion of each curve to the right of the critical ordinate, the most favourable conditions for the observation of the

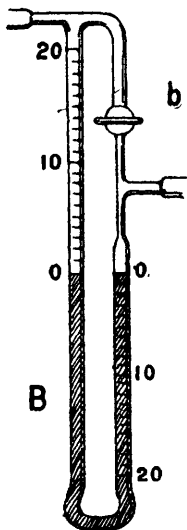
phenomenon being when this portion is greatest. In the mixtures examined, this is the case for those containing 32.2 and 40.4 per cent. of methyl chloride, where it occurs within temperature limits of 5°. Where comparable, the results are in good accord with those of Kuenen, as is seen by the comparison of the author's results for the mixture containing 59 per cent. methyl chloride with Kuenen's results for the mixture containing 61 per cent. of the same compound.

L. M. J.

Deviations from Boyle's Law of Mixtures of Hydrogen and Carbon Dioxide. By J. E. VERSCHAFFELT (*Zeit. physikal. Chem.*, 1899, 31, 97—102).—For mixtures of hydrogen and carbon dioxide, the author finds that the values of the coefficient m_1 in the equation: $pv = RT + m_1/v + m_2/v^2 + \dots$, can be calculated from the formula: $m_1 = 0.00074x^2 - 0.0012x(1-x) - 0.0063(1-x)^2$, where x represents the ratio of the number of hydrogen molecules to the total number of molecules of the mixture. The experimental numbers for m_1 show good agreement with the calculated values.

At 18°, mixtures of these gases obey to the second approximation the law: $pv = 1.067 + m_1/v = 1.067(1 + 1/v \cdot m_1/1.067)$; the expression within the brackets, which is equal to $1.00069x^2 + 1.9989x(1-x) + 0.9941(1-x)^2$, is greater than unity for hydrogen (that is, when $x=1$) less than unity for carbon dioxide ($x=0$), and equal to unity for the value $x=0.795$. So that for a mixture of composition represented by this value of x , Boyle's law is obeyed to the second approximation.

T. H. P.



Determination of Vapour Density under Arbitrary Pressure. II. By OTTO BLEIER and LEOPOLD KOHN (*Monatsh.*, 1899, 20, 909—925. Compare Abstr., 1899, ii, 643).—Several improvements in this method are announced. Instead of an air-pump, it is now recommended that a mercury pump should be used, so that the determination may be started under a pressure of only 2—3 mm. The bulb in which the vaporisation of the substance takes place should be of 400—500 c.c. capacity. Determinations can be carried out in which the increment of pressure is only about 5 mm. Such small increments of pressure are not conveniently measured by means of the manometer previously described (*loc. cit.*), which is replaced by the special form of differential manometer here figured. It is filled with paraffin oil instead of mercury, so that the "difference" on the manometer is about 17 times as great as

it would be were mercury used and can be easily read off by the unaided eye. The upper end of this manometer is attached to a large flask which is provided with two stopcocks and an ordinary manometer and acts as a "vacuum reservoir." Determinations are carried out as follows: The substance is first placed in the neck of the bulb, which is then

heated in the required bath. The apparatus, with the stopcock of the manometer open, is then exhausted by the pump till the required diminution of pressure is obtained. The stopcock of the manometer is then closed and that of the vacuum reservoir opened (this reservoir having been previously exhausted). The substance is allowed to fall into the bulb and the "increment" of pressure occasioned by its vaporisation is directly read off after an interval of not more than 4 minutes. The air is let into the apparatus again by means of a slit in the stopcock between the "reservoir" and the manometer, which in one position allows air to pass into the manometer, but not into the "reservoir."

This procedure further appears to afford a means of determining whether a substance undergoes dissociation, for in such cases the increment of pressure is only slowly, whilst in normal cases it is rapidly (1—4 min.), shown.

The results of the large number of determinations quoted, using baths of water, toluene, xylene, and aniline, all agreed with the theoretical value to within 2 per cent.

R. H. P.

New Pyknometer for the Determination of the Specific Gravity of Light Liquids. By HEINRICH GÖCKEL (*Zeit. angew. Chem.*, 1899, 1194—1195).—This is a pyknometer bulb, sealed to a massive glass foot, which supports the instrument in an upright position when placed in water in order to acquire a definite temperature. L. DE K.

Molecular Volume of Camphor Derivatives. By ALBIN HALLER and PAUL TH. MÜLLER (*Compt. rend.*, 1900, 130, 221—224. Compare Abstr., 1899, i, 622, and this vol., i, 182).—The molecular volumes of a series of camphor derivatives dissolved to a $N/4$ solution in toluene were obtained by direct experiment and by the employment of the following expression: $V = M + S/d - S/d'$, where M , is the molecular weight of the compound, S the weight of solvent containing one molecular proportion of the dissolved substance, and d and d' the specific gravities of the solution and solvent respectively. These constants may also be calculated from Traube's formula, $V = \Sigma a - N - L + C$, where N is a coefficient depending on the number of hexamethylene rings in the molecule, L a coefficient proportional to the double linkings, C the co-volume, and Σa the sum of the atomic coefficients. It is found that the calculated values are always greater than those obtained by experiment, the difference being the sum of the decrements due to the closed chains other than hexamethylene rings present in the molecule.

In the case of methyl camphorate which contains one additional ring, the decrement is 17.6, whilst with camphor, borneol, methyl camphor-carbonate, benzylidenecamphor, benzylcamphor and their homologues, the mean value of the decrement due to two camphor nuclei is 23, the extremes being 20.6 and 25.4. Piperonylidenecamphor and piperonylcamphor contain, in addition to the camphor nuclei, an additional piperonylic ring; this increases the decrement by 6 units, the mean value of this coefficient being 29.

Bornyl succinate contains two camphor residues, and the decrement

is 33.2; this result indicates that the effect produced by four closed chains is not double that produced by two, and therefore the law of the addition of nuclear decrements is not absolutely general. G. T. M.

Surface Tension of Organic Liquids. By PAUL DUTOIT and LOUIS FRIDERICH (*Compt. rend.*, 1900, 130, 327—330. Compare Abstr., 1899, ii, 350).—The following values of k , the temperature coefficient of molecular surface energy, were determined by the method of Ramsay and Shields:

m-Xylene, 2.20; mesitylene, 2.15; durene, 2.14; pentamethylbenzene, 2.165; aniline, 1.60—2.05; methylaniline, 1.99—2.08; ethylaniline, 2.22; dimethylaniline, 2.39; diethylaniline, 2.34; *o*-toluidine, 2.05; *p*-toluidine, 1.72; dimethyl-*o*-toluidine, 2.53; diphenylamine, 2.57; acetonitrile, 1.50—1.56; propionitrile, 1.67—1.74; butyronitrile, 1.89; *p*-toluonitrile, 1.88—2.05; hexane, 2.11; diphenyl, 2.22; naphthalene, 2.29; acenaphthene, 2.31; diphenylmethane, 2.25; *s*-diphenylethane, 2.49; pyridine, 2.17; quinoline, 2.43; acetone, 1.83; methyl ethyl ketone, 1.85; acetophenone, 2.14; benzophenone, 2.63.

The following conclusions are drawn: (1) the value of k varies with the temperature for abnormal liquids, but not for normal liquids; (2) for normal liquids, the value of k is not constant, but varies within limits the range of which is greater than was formerly supposed. H. R. LE S.

Nernst's Osmotic Experiment and a Definition of Osmotic Pressure. By A. CRUM BROWN (*Proc. Roy. Soc. Edin.*, 1899, 22, 439—440).—An osmotic cell of Nernst's type (Abstr., 1890, 1365) may be formed with three liquid layers as follows: (1) water + phenol + calcium nitrate, (2) phenol + water, (3) water + phenol. If (1) is lowermost, and (2) lies above it, then the layer (2), being impermeable for calcium nitrate, gradually rises as water diffuses from (3) to (1).

If two partially miscible liquids A and B are shaken up under the pressure p , and a given solution of a substance N in A is shaken up with B under the pressure p' , the solutions of A in B formed in the two cases will have the same concentration if $p' - p$ is equal to the osmotic pressure. J. C. P.

Theory of Diffusion. By OTTO WIEDEBURG (*Zeit. physikal. Chem.*, 1899, 30, 586—592).—The author criticises certain tacit assumptions in Bose's paper on the "Theory of Diffusion" (Abstr., 1899, ii, 729), and deduces other expressions. For sufficiently low concentrations, these reduce to one previously obtained empirically, $D = D_0(1 + \gamma c)$, where D_0 and γ are constants, the latter being capable of positive or negative values as the diffusion coefficient may either decrease or increase with dilution. The value for D_0 is $RT.2uv/u + v$, where u and v are the velocity of anion and cation respectively; γ has the value $2/k \cdot \{w(u + v)/2uv - 1\}$ where w is the velocity of the undissociated molecule and k the dissociation constant. When γ and k are small, therefore $1/w = \frac{1}{2}(1/u + 1/v)$ and is otherwise calculable where the other constants are known. The values of w and of D_0 are so

calculated for copper sulphate, but the results do not agree with those obtained by extrapolation from measurements of the diffusion.

L. M. J.

Osmotic Pressure of Concentrated Solutions. By THOMAS EWAN (*Zeit. physikal. Chem.*, 1899, 31, 22—34).—When P is the osmotic pressure at the temperature T of a solution of 1 gram of sucrose in m grams of water, thermodynamical considerations lead to the relation:— $Pv_0/JT = W_0(1/F - 1/T_0) - c/2.(T_0 - F)^2/F^2 - dQ_T/dm.(1/F - 1/T) + C_L/2.(T - F)^2/F^2$, where v_0 is the increase of volume accompanying dilution, J the mechanical equivalent of heat, F the freezing point of the solution, W_0 the latent heat of fusion of water at its freezing point T_0 , c the difference between the specific heats of water and ice, dQ/dm the heat of dilution, and C_L the temperature coefficient of the heat of dilution.

The freezing points of several sucrose solutions containing from 30—70 grams of sucrose per 100 grams of water have been carefully determined. The molecular depressions obtained are satisfactorily given by the equation $t/g.342 = 18.58 + 0.97t$, where t is the depression of the freezing point in a solution containing g grams of sucrose in 100 grams of water. The formula gives values about 1 per cent. smaller than those of Raoult (*Abstr.*, 1899, ii, 203).

As regards the heat of dilution, it is found that if Q be the heat developed when a solution of 1 gram of sucrose in 0.6051 gram of water is diluted until it contains m grams of water to 1 gram of sucrose at about 14° , $Q = 1.25(m - 0.6051)/(0.6 + m)$, whence $dQ/dm = 1.506/(0.6 + m)^2$. Equations are also given for calculating the temperature coefficient of dQ/dm and v_0 .

Of various empirical formulæ representing $(dP/dT)_v$ as a function of the concentration, the most satisfactory was found to be $(dP/dT)_v = R/[V - (V - nM_0v_0)/m]$, where V is the volume of solution containing 342 grams of sucrose and nM_0 grams of water; nM_0v_0 is the increase of volume that would occur if nM_0 grams of water were added to the solution without appreciably changing its concentration. $V - nM_0v_0$ is a measure of the volume occupied by the sucrose, and experiment shows it to be nearly constant: the quantity $(V - nM_0v_0)/m$ corresponds with the b of van der Waals's equation.

On the supposition that the dissolved substance does not polymerise or dissociate, an expression is obtained for calculating the molecular weight from the freezing point depression in a concentrated solution; with this expression, values are obtained for the molecular weight of sucrose not differing greatly from 342.

J. C. P.

Hydrates in Solution. By WILDER D. BANCROFT (*J. Physical Chem.*, 1899, 3, 551—554).—Nernst, in his "Theoretische Chemie," considers only very briefly the case in which the solvent actually takes part in the reaction, and there deduces that, in a dilute solution, the percentage of the hydrated substance is independent of concentration. This, however, only holds when no secondary electrolytic dissociation takes place, and the author therefore extends the case to hydrated salts. If A be the total concentration of the salt, c that of the water x the anhydrous dissociated salt, and y the amount of dissociated salt,

the equilibrium equations are (for a binary salt) $Kx/v = (y/v)^2$ (1); $K_1(A - x - y)/V = x/v \cdot (c/v)^n$ (2); hence by regarding c/v as constant, that is, for dilute solutions, is obtained $K_3(A - x - y)v = (y/v)^2$ (3), from which follows a decrease of hydration by dilution, so that hydrated salts are decomposed by water. By combination of (1) and (3), with elimination of x , there results $K_4(A - y)/v = (y/v)^2$, which is the ordinary dilution law of Ostwald; so that this law is valid for hydrated salts, and the variations are not accounted for by the assumption of hydrates. Cases are considered also where one ion is hydrated, or where only the hydrated salt is an electrolyte, but no essential difference results.

L. M. J.

Solid Solutions and Isomorphous Mixtures. By GIUSEPPE BRUNI (*Real Accad. Lincei*, 1899, [v], 8, ii, 212—219).—A polemical paper in which Bodländer and Küster's views concerning the different behaviour of solid solutions and isomorphous mixtures are combated.

T. H. P.

Reciprocal Solubility of Liquids. By GIUSEPPE BRUNI (*Real. Accad. Lincei*, 1899, [v], 8, ii, 141—149).—The author has studied the mutual solubility of water and methyl ethyl ketone in presence of 1.5 per cent. of alcohol. The curve obtained, which is the section of the dineric surface by a plane parallel to one side of the triangular diagram, is closed and shows that mixtures of water and methyl ethyl ketone in presence of 1.5 per cent. of alcohol can only form two distinct layers at temperatures lying between $+16^\circ$ and $+148^\circ$. For the upper part of the curve, the diameter parallel to the axis of concentrations is nearly a straight line, whilst for the lower portion this is no longer the case.

The freezing point curve for the same mixture has also been determined and is found to have no point in common with the liquid solubility curve. This has never before been observed with curves representing states of stable equilibrium.

T. H. P.

Solubility of Ethyl Acetate in Aqueous Salt Solutions. By HANS EULER (*Zeit. physikal. Chem.*, 1899, 31, 360—369).—Ethyl acetate is less soluble in salt solutions than in pure water. The equivalent diminution of solubility is represented by the expression $(0.825 - l)/m$, where 0.825 is the solubility (in gram-molecules per litre) of ethyl acetate in pure water at 28° , and l its solubility in a salt solution of the concentration m . The value of this expression has been determined for a number of salt solutions of various concentration, and the results resemble those obtained by Roth for the solubility of gases in salt solutions (*Abstr.*, 1898, ii, 18). Thus the equivalent diminution of solubility increases with the dilution of the salt solution, and when the various salts are arranged according to their values for the above expression, the order is the same whether the dissolved substance be hydrogen, nitrous oxide, or ethyl acetate. Comparison of the results obtained in these three cases shows that the percentage diminution of solubility increases with the solubility of the compound investigated.

J. C. P.

Gibbs' Phase Rule. By C. H. WIND (*Zeit. physikal. Chem.*, 1899, 31, 390—397).—A proof of the phase rule, not suitable for abstraction. The author claims to have arrived at a clear formulation of the phase rule with a minimum of initial hypothesis. J. C. P.

Application of the Phase Rule to Alloys and Rocks. By HENRI LE CHATELIER (*Compt. rend.*, 1900, 130, 85—87).—The successive reversible changes which a mixture of molten solids may experience during cooling at constant pressure, such as solidification, crystallisation, separation of solid phases, &c., must finally lead to a univariant system, in which the number of phases is equal to the number of independent constituents, and as an example the cooling of a molten mixture of iron and carbon is considered. As a natural example, granite is cited; here the independent constituents are three in number—silica, alumina, and potash, whilst three phases are also present, namely, quartz, felspar, and mica. If, in a mass thus obtained, there is present a greater number of phases, then the operations leading to its formation are not reversible and the mass is not in stable equilibrium. The principal cause of such unstable systems is too rapid cooling and in alloys a characteristic is that the properties are very variable and dependent on the conditions of preparation.

L. M. J.

Physical Equilibrium in Mixtures of Isomorphous Substances. By GIUSEPPE BRUNI and F. GORNI (*Real. Accad. Lincei*, 1899, 8, ii, 181—190. Compare Abstr., 1899, ii, 356, and 731).—Freezing point curves have been traced for the following mixtures of isomorphous compounds. (1) *p*-Dichlorobenzene (m. p. 52·7°) and *p*-chlorobromobenzene (m. p. 67·0°). (2) *p*-Dichlorobenzene and *p*-dibromobenzene (m. p. 85·9°). In each of these cases, the gradual addition of the component of higher melting point to the other causes, firstly, a lowering of the freezing point, which afterwards rises, the curves being continuous. (3) *p*-Chlorobromobenzene and *p*-dibromobenzene. In this case, the freezing point rises continuously when the component of higher melting point is added to the other. (4) Azobenzene and dibenzyl. On adding azobenzene to dibenzyl, depression of the freezing point takes place until about 30 per cent. of the former is present, after which the curve runs horizontally for some distance and then rises.

Mixtures of cinnamic and phenylpropionic acids give a freezing point curve similar to that given by most isomorphous mixtures, although these acids have crystalline forms which are in no way simply related.

It is concluded that no difference in kind, but only in degree, exists between the freezing point curves of isomorphous mixtures and those of solid solutions of non-isomorphous substances.

The following crystallographic data, from measurements by G. Boeris, are given. *p*-Dibromobenzene : monoclinic [$a : b : c = 2\cdot6660 : 1 : 1\cdot4179$. $\beta = 67^\circ 22'$]. *p*-Chlorobromobenzene : monoclinic [$a : b : c = 2\cdot6077 : 1 : 1\cdot4242$. $\beta = 67^\circ 0'$]. Phenylpropionic acid : monoclinic [$a : b : c = 1\cdot6054 : 1 : 0\cdot5552$. $\beta = 78^\circ 47'$].

T. H. P.

Equilibrium between Sulphuric Acid and Sulphates in Aqueous Solution. By SYDNEY A. KAY (*Proc. Roy. Soc. Edin.*, 1899, 22, 484—522).—The amount of free acid in a mixed solution of sulphuric acid and a normal sulphate has been determined by measuring the rate of catalysis of ethyl acetate, a correction being applied for the influence of the normal salt on the catalytic action of the acid.

The equilibrium may be represented by an equation of the form $[c_1(1 - a_1)]^{0.85}/[c_3(1 - a_3)] = A/[c_2(1 - a_2)]^x$, where c_1, c_2, c_3 are the total concentrations of sulphuric acid, normal sulphate, and acid sulphate respectively, and a_1, a_2 , and a_3 the corresponding degrees of dissociation; x is equal to unity for potassium sulphate, and has the value 1.35 for sodium and lithium sulphates. The constant A has a characteristic value in each case, and in the expressions involving potassium, sodium, and lithium sulphates has the values 0.259, 0.0618, and 0.060. The expression gives results agreeing well with those actually observed.

J. C. P.

Reciprocal Salt Pairs. II. Equilibrium Phenomena in Presence of a Double Salt. By WILHELM MEYERHOFFER and A. P. SAUNDERS (*Zeit. physikal. Chem.*, 1899, 31, 370—389).—A continuation and expansion of the work recorded in an earlier paper (*Abstr.*, 1899, ii, 410). The change of the system $K_3Na(SO_4)_2 + NaCl + Na_2SO_4 \cdot 10H_2O$ at 16.3°, consisting in a dehydration of the sodium sulphate, is fully considered, and the conditions of existence of hydrated sodium sulphate determined and graphically represented. Distinction is drawn between congruent and incongruent cryohydrates; the former solidify regularly, whether solid is present or not, whilst with the latter, the presence of a certain quantity of solid salt is necessary.

It is pointed out that, in many cases of secondary transition, a better review of the phenomena is secured by the use of van't Hoff's theory than by the application of the phase rule.

J. C. P.

Characteristics of certain Chemical Reactions. By JOHN GIBSON (*Proc. Roy. Soc. Edin.*, 1898, 22, 33—37).—The chemical behaviour of hydrochloric, nitric, and sulphuric acids is shown to differ in several special cases, according as the acid is above or below the strength corresponding with maximum conductivity. The author reviews the general connection between chemical reactions and conductivity, and states as a working hypothesis that the degradation of potential chemical energy is generally associated with molecular rearrangement involving diminished electrical resistance.

J. C. P.

Velocity of Graded Actions. By JAMES WALKER (*Proc. Roy. Soc. Edin.*, 1898, 22, 22—32).—When a reaction takes place in two stages, the theory of mass action in its usual form will be applicable only if one stage of the reaction takes place in a very short time as compared with the other. Otherwise it may be shown that, when the two reactions involved are non-reversible and unimolecular,

$$z = A\{1 + ne^{-mt}/(m - n) + me^{-nt}/(n - m)\},$$

where z is the quantity of the final substance, and m and n are the velocity constants of the two separate reactions. The error introduced by calculating z as if the reaction took place in one stage instead of two, depends, of course, on the relative value of m and n , and for the relation $n = 100m$ is of small account except at the beginning of the action.

J. C. P.

Numerical Laws of Chemical Equilibrium. By OCTAVE BOUDOUARD (*Compt. rend.*, 1900, 130, 132—134).—In a gaseous system in equilibrium there exists at all temperatures and pressures a relation between the concentration of the various gaseous phases which is

given by the equation $RT \int L.dT/T^2 + N \log P + \log c^n c_1^{n_1} \dots / C^m C_1^{m_1} \dots =$

constant where L is the heat of reaction, P the total pressure, $c, c_1 \dots$ the concentration of the reaction gases, $C, C_1 \dots$ that of the products, $n, n_1 \dots m, m_1 \dots$ the numbers of the reacting and produced molecules, and N the sum $n + n_1 + \dots - m - m_1 \dots$. In the case of the system, carbon dioxide, carbon monoxide, and carbon, the final equilibrium does not depend on the initial state between 650° and 800° , and the expression reduces in this case to $-21000/T + \log c/C^2 = \text{constant}$, ($L = 42$ Cals.). From this, the ratios of the concentration of the two oxides at various temperatures are calculated, the agreement of result with experimental determinations being seen in the following table:

Temp.	Carbon dioxide.		Carbon monoxide.	
	Found.	Calc.	Found.	Calc.
650°	0.61	0.61	0.39	0.39
800	0.07	0.10	0.93	0.90
925	0.04	0.03	0.96	0.97

L. M. J.

Kinetics of Reactions with Auxiliary Reactions. By RUDOLF WEGSCHIEDER (*Zeit. physikal. Chem.*, 1899, 30, 593—600).—In the *Lehrbuch der Allgemeinen Chemie*, 2, ii, 247 *et seq.*, Ostwald considers the case of reaction, accompanied by collateral reactions, that is, a reaction in which two distinct sets of products result, but the cases examined are specially chosen as simplified examples, and in each lead to but one differential equation for the reaction velocity. The author considers the case more fully, and shows that in general there are as many differential equations needed as there are collateral reactions. The ratio of the sets of products is also in general a time function, but is constant in those cases in which the left sides of the equations representing the various reactions are identical, and the observation of this constancy is a sufficient proof of this identity obtaining.

L. M. J.

Velocities of Reaction. By ALEXANDRE DE HEMPTINNE (*Zeit. physikal. Chem.*, 1899, 31, 35—41).—Velocity constants are given for the hydrolysis of methyl acetate by mixtures of varying composition of hydrochloric acid and acetone, together with the electrical conductivities of the different mixtures. The velocity constant and the conductivity both decrease as the proportion of hydrochloric acid present decreases, but not to the same degree, the ratio of speed to conductivity increasing. Thus, besides the ionic action, the solvent exerts

further action on the velocity of hydrolysis, and, in the case of acetone this action is catalytic, since acetone has no action either on methyl acetate, or its products of hydrolysis.

In presence of glycerol, neither hydrochloric nor sulphuric acid gives constant velocity numbers for the hydrolysis of methyl acetate; the promotion of the hydrolysis by glycerol depends on the slight affinity the latter possesses for the acetic acid produced. T. H. P.

Velocity of Reaction in Heterogeneous Systems. By HEINRICH GOLDSCHMIDT [with ANTON MISSERSCHMITT] (*Zeit. physikal. Chem.*, 1899, 31, 235—249).—The difficulty of keeping a solution saturated with a slightly soluble substance in a heterogeneous system may be avoided by dissolving the substance in a liquid which does not mix with the solvent used; experience shows that in this case equilibrium is rapidly established between the two solutions.

The author has examined the rate of hydrolysis of ethyl acetate by dilute hydrochloric acid, dissolving the ester in benzene, and shaking the benzene solution with the hydrochloric acid solution. The equation for the velocity constant is $k = 1/t \cdot (v_2 + v_1 C) / v_1 C \cdot \log a / (a - x)$, where a is the initial quantity of ester, x the acetic acid formed after time t , v_1 and v_2 the volumes of hydrochloric acid and benzene respectively, and C ($= 0.079$) the partition coefficient of ethyl acetate between water and benzene. The values of k calculated with this equation are fairly constant, but show a tendency to fall with the time. This is accounted for by the action not going completely from left to right of the equation, a small quantity of the ester remaining undecomposed in the benzene. When allowance is made for this, a very satisfactory series of values is obtained for the constant.

A bimolecular reaction, the hydrolysis of ethyl acetate with baryta, has also been studied in a similar way. The velocity constant was found to have the same value as in a homogeneous system, provided the concentrations of the reacting substances were not over $1/20$ th normal. J. C. P.

The Velocity of Reaction before complete Equilibrium and before Transition Points. True meaning of the Law of Chemical Equilibrium of Heterogeneous Systems. Reactions in Heterogeneous Systems. By MEYER WILDERMANN (*Zeit. physikal. Chem.*, 1899, 30, 341—382).—See *Proc.*, 1899, 15, 175.

Influence of Catalytic Agents on the Oxidation of Oxalic Acid Solutions. By W. P. JORISSEN and LODIEWYK TH. REICHER (*Zeit. physikal. Chem.*, 1899, 31, 142—163).—The paper contains a full review of investigations hitherto published on the influence of catalytic agents on oxidation generally. Experiments made by the authors show that in diffuse light the oxidation of oxalic acid solutions is accelerated by the presence of iron, chromium, cerium, thorium, and erbium sulphates, sodium fluoride, and manganese sulphate, acetate, butyrate, benzoate, and oxalate. Potassium, magnesium, and yttrium sulphates have no accelerating influence. In sunlight, manganese sulphate, oxalate, acetate, butyrate, and benzoate increase the rate of oxidation. The extent of the acceleration depends on the nature of

the catalytic agent and grows with the concentration of the latter. The accelerated oxidation of oxalic acid, due to manganese salts, cannot be accounted for by the formation of manganese oxalate, which is much more slowly oxidised than oxalic acid itself. J. C. P.

Change in the Strength of Weak Acids by the Addition of Salts. By SVANTE ARRHENIUS (*Zeit. physikal. Chem.*, 1899, 31, 197—229).—When normal salts in small quantity are added to solutions of acetic, formic, and phosphoric acids, the inversion of sugar by these acids is accelerated; the amount of acceleration depends on the quantity of salt added, and is independent of the nature of the salt, although sodium bromide and potassium chlorate behave exceptionally. The observed acceleration is corrected (1) for the effect of the normal salt itself on the inversion, (2) for the formation by double decomposition of new undissociated electrolytes. Both corrections are small when the concentration of the salt solution added is small. After these two factors have been allowed for, it is seen that the addition of the normal salt increases the dissociation constant of the weak acid—exactly what happens in the case of an ordinary salt solution; further addition of salt, that is, increase of concentration, increases the dissociation constant, so that normal salts, strong acids, and bases do not obey Ostwald's dilution law.

The correction applied in conductivity experiments for the conductivity of the solvent water is probably too small, for the dissociation of the carbonic acid contained in the water would, in view of the above results, be much increased on the addition of salts. If this is so, the degree of dissociation of a salt, as hitherto calculated from the conductivity, is too small. The author points out that Noyes' method of calculating the conductivity of a mixed salt solution from that of the separate solutions leads to results at variance with observation; experiment, on the other hand, confirms the view that the conductivity of an electrolyte depends only on the total number of ions per litre (see Abstr., 1888, 1144). The author holds that Noyes' method of calculating the diminution of solubility of a salt on the addition of one of its ions to the saturated solution must be given up; experiments with the sodium and silver salts of fatty acids show that the undissociated portion of the sparingly soluble salt is by no means constant, as has hitherto been assumed. In these experiments, it was found that the first addition of the sodium salt had a much greater effect on the solubility of the silver salt than the later additions. J. C. P.

Nature of Soap Emulsions. By FREDERICK G. DONNAN (*Zeit. physikal. Chem.*, 1899, 31, 42—49).—When oil drops are allowed to ascend from a pipette through an alkaline liquid, the number of drops formed from a given volume of oil increases rapidly with the concentration of the alkali, owing to the diminution of surface tension caused by the formation of a soap. Commercial oils, which exhibit this phenomenon, have an acid reaction, and if the oil be first purified, the number of ascending drops is practically the same in N/1000 NaOH solution as in pure water. Solutions of fatty acids in a pure neutral hydrocarbon of the paraffin series behave similarly to

the commercial oils; the number of drops formed depends on the concentration of the acid as well as of the alkali, although the lower fatty acids are without action at all. The diminution of surface tension due to the salts of the higher fatty acids was confirmed by comparing the levels in a U-tube of two contiguous hydrocarbon and alkaline solutions.

The peculiar boiling phenomena of soap solutions, investigated by Krafft (Abstr., 1896, i, 80; ii, 468), cannot in the light of the above experiments be attributed to high surface tension, as has been done by Kahlenberg and Schreiner (Abstr., 1899, ii, 202), but is due to the frothing of the liquid, as shown by Lord Rayleigh.

It appears that the soap is concentrated in the layer between oil and aqueous solution, with the effect that the formation of small drops is favoured. The stability of an emulsion is due to this concentrated surface layer resisting the union of the already existing small drops; from this point of view, emulsions are akin to frothing, and it is suggested that froth is a sort of air emulsion. J. C. P.

Experiments on Adsorption. By JOHANNES G. C. VRIENS. (*Zeit. physikal. Chem.*, 1899, 31, 230—234).—When a centinormal solution of nitric acid is run through a number of filter papers successively, the concentration diminishes, and the fall of concentration, as determined by the change in conductivity, is proportional to the number of filters. J. C. P.

Inorganic Chemistry.

Distillation of Water. By W. MAREK (*J. pr. Chem.*, 1899, [ii], 60, 582—584).—The apparatus described is for the preparation of moderately large quantities of specially pure distilled water; it consists of a copper still of some 36 litres capacity internally tinned and fitted with a tin head and worm. The various parts are joined by flanges which are ground into one another, so that no organic or inorganic cementing material is required. Ordinary distilled water (30 litres) is introduced and is boiled for several minutes before the worm is cooled, 0.3 gram of potassium permanganate in concentrated aqueous solution is introduced, and the distillation carried out in the ordinary manner; the first 3 litres are rejected and the following 18 litres collected in large glass bottles previously treated with nitric acid. The flame employed is small, and the whole operation requires some 15 hours. J. J. S.

Nature of Water of Crystallisation. By FRIEDRICH RINNE (*Jahrb. f. Min.*, 1899, i, 1—31).—The water of crystallisation of a salt behaves in many ways like ordinary free water; for example, it gradually evaporates, especially at a slightly elevated temperature,

and in some salts there are certain points analogous to the boiling point of ordinary water. Copper sulphate ($\text{CuSO}_4 + 5\text{H}_2\text{O}$), when quickly heated, gradually rises in temperature to 105° , and remains at this temperature until $2\text{H}_2\text{O}$ has been expelled; the temperature then again gradually rises to 117° , when the boiling point of the second $2\text{H}_2\text{O}$ is reached; the boiling point of the last H_2O is 258° . A less sharply marked point is 99° , where $\frac{1}{2}\text{H}_2\text{O}$ is lost. For barium chloride ($\text{BaCl}_2 + 2\text{H}_2\text{O}$), the boiling point of each molecule of water is 105° and 162° . These boiling points vary with the atmospheric pressure.

Heulandite and stilbite are examples of another group of substances in which the water of crystallisation behaves in a different manner; here, there is nothing analogous to boiling point, the water being lost gradually and *pari passu* with the rise in temperature; at the same time, there is a gradual change in the optical orientation of the crystals (Abstr., 1896, ii, 368; 1897, ii, 327). The amount of water lost at any particular temperature is less the greater the atmospheric pressure and the greater the amount of moisture in the air.

In these two groups, the relation of the water of crystallisation to the salt can be considered to be, in the first case, that of a molecular compound, and, in the second, that of a solid solution. L. J. S.

Action of Persulphates on Iodine. By HUGH MARSHALL (*Proc. Roy. Soc. Edin.*, 1898, 22, 388—390).—When solutions of potassium iodide and potassium persulphate are mixed and warmed, iodine is liberated; investigation shows that this iodine is oxidised to iodic acid by excess of persulphate. If iodine is digested in a loosely corked flask at a moderate temperature with a strong solution of ammonium persulphate, the iodine gradually dissolves, and crystalline ammonium hydrogen iodate is obtained. In Price's experiments on the reaction between potassium iodide and potassium persulphate (Abstr., 1899, ii, 147), there may have been catalytic action, the iodine being alternately oxidised by the persulphate, and reduced by hydriodic acid. J. C. P.

Vapour Density of Sulphur. By OTTO BLEIER and LEOPOLD KOHN (*Ber.*, 1900, 33, 50—51. Compare Biltz, Abstr., 1888, 1027; 1889, 340; Biltz and Meyer, 1889, 674; Krause and Meyer, 1890, 1365; Riecke, 1891, 381; Schall, 1889, 331.—The following results have been obtained with the aid of the apparatus previously described (Abstr., 1899, ii, 643):

<i>t</i>	310°	262°	236°	212°	193°
<i>p</i>	42.6	15.0	9.4	4.2	2.1
$D(\text{O}_2 = 1)$	7.44	7.5	7.66	7.80	7.85

from which it follows that the undissociated sulphur molecule consists of eight atoms. J. J. S.

Hyposulphurous Acid. By AUGUST BERNTHSEN and MAX BAZLEN (*Ber.*, 1900, 33, 126—132. Compare Abstr., 1881, 508, 976).—By passing sulphur dioxide into a solution of sodium hydrogen sulphite in contact with zinc, it is converted quantitatively into the

hyposulphite according to the equation $2\text{NaHSO}_3 + \text{SO}_2 + \text{Zn} = (\text{Na}_2\text{S}_2\text{O}_4 + \text{ZnSO}_3) + \text{H}_2\text{O}$; by adding chalk, the zinc sulphite can be removed, and a solution of sp. gr. 15—16° Bé. obtained, which will reduce a fifth of its weight of indigo. From this solution, the sodium hyposulphite separates in crystals on adding salt or sodium hydroxide, and when washed with aqueous, and then with dry acetone, has the composition $\text{Na}_2\text{S}_2\text{O}_4 + 2\text{H}_2\text{O}$, thus confirming the authors' earlier conclusions, and disproving the formula NaHSO_2 given to the salt by Schützenberger [compare Nabl's zinc salt, ZnS_2O_4 (this vol., ii, 13)]; Grossmann's acid salts (*J. Soc. Chem. Ind.*, 1898, 17, 1109; 1899, 18, 452—453) cannot be prepared from the pure material, as sodium hyposulphite solutions deposit sulphur on adding a single drop of acid. Sodium hyposulphite forms large, thin, glistening prisms, which are fairly stable, but gradually effloresce and oxidise to sodium pyrosulphite, $\text{Na}_2\text{S}_2\text{O}_5$; the dry salt is more stable, but when heated to dull redness burns with a blue flame and liberates sulphur dioxide.

T. M. L.

Oxidation of Hydroxylamine. By GEORG VON KNORRE and KURT ARNDT (*Ber.*, 1900, 33, 30—42).—Either the acid hydroxylamine solution, or the oxidising solution, was boiled in a stout conical flask fitted with a funnel and a delivery tube until the air was expelled; the flask was then connected with a vessel filled with mercury, the second solution (freed from dissolved gas by boiling) was run in, and the gas evolved driven over by boiling into the vessel mentioned, transferred from this to a gas burette, and analysed. The oxidising agents tried were potassium nitrate and sulphuric or hydrochloric acid; hydrated manganese peroxide, potassium permanganate, potassium dichromate, vanadic acid, and potassium persulphate, all with sulphuric acid; alkaline copper sulphate and mercuric chloride; also hydrogen peroxide. Nitrous oxide is usually the main product, but nitric oxide is often mixed with it, and the solution nearly always contains nitric (or nitrous) acid. The relative amounts of the two oxides vary with the oxidising agent and with the concentration of the latter. With vanadic acid, the gas consists chiefly of nitrogen; with potassium persulphate, it is pure oxygen, and also with hydrogen peroxide, but in the last case only a small amount is formed.

C. F. B.

Action of very dilute Nitric Acid [on Metals]. By A. VAN BIJLERT (*Zeit. physikal. Chem.*, 1899, 31, 103—113).—The products of the action of nitric acid on metals result from (1) the oxidising action of the non-dissociated portion of the acid, and (2) the reducing action brought about by the dissociated acid. The oxidising action is hence the greater the stronger the acid, and the reducing action is more evident when weaker acid is employed. For the metals magnesium, zinc, or cadmium the reaction, $2\text{M} + 2\text{HNO}_3 \cdot \text{Aq} = 2\text{MNO}_3 \cdot \text{Aq} + \text{H}_2$, is exothermic, and ammonium nitrate is among the products obtained; whilst, for copper, silver, or mercury, this decomposition absorbs heat, and in these cases no ammonium nitrate is found.

A series of experiments on the action of dilute nitric acid (*N*/20 to *N*/10) on zinc at about 25° shows that the amount of ammonia formed,

bears to the amount of zinc used, a ratio varying from 1 : 33 to 1 : 40, the ratio required by the equation $4\text{Zn} + 10\text{HNO}_3 = 4\text{Zn}(\text{NO}_3)_2 + \text{NH}_4\text{NO}_3 + 3\text{H}_2\text{O}$ being 1 : 15 or 16. This deviation is ascribed to the intermediate formation of the other reduction products, such as nitrous acid, nitric oxide, nitrogen, &c. No hydroxylamine was detected.

T. H. P.

Spontaneous Combustion of Coal. By RUD. GRIMM (*Zeit. angew. Chem.*, 1899, 1242).—A heap of slag containing furnace ashes mixed with a small proportion of unconsumed coal, became ignited internally on being left exposed to the air, probably owing to the presence in the interior of a small quantity of still glowing clinker; the outer crust of the heap was riven, and clouds of steam were evolved. In the rents so formed, large, rhombic crystals of sulphur and crusts of ammonium chloride were observed; the author explains the liberation of sulphur thus: $\text{FeS} + \text{H}_2\text{O} = \text{H}_2\text{S} + \text{FeO}$; $2\text{H}_2\text{S} + \text{SO}_2$ (from FeS_2) = $3\text{S} + 2\text{H}_2\text{O}$.

W. A. D.

Solubility of Argon and Helium in Water. By TADEUSZ ESTREICHER (*Zeit. physikal. Chem.*, 1899, 31, 176—187).—The absorption coefficient of argon is 0.05612 at 1°, and 0.02567 at 50°, falling regularly between those temperatures. The absorption coefficient of helium is 0.01487 at 0.5°, and 0.01404 at 50°, but at 25° it has a minimum value 0.01371; these values are about twice as large as that provisionally given by Ramsay, namely, 0.0073 at 18.2°. The minimum solubility of helium seems to be connected with the difficulty of liquefaction, for the solubility curve of hydrogen shows the same peculiarity (compare Abstr., 1892, 107); other gases with a higher critical temperature will probably be found to have a minimum solubility above 100°.

A full account is given of the apparatus and method employed.

J. C. P.

Electrolysis of Potassium Chloride. By ANDRÉ BROCHET (*Compt. rend.*, 1900, 130, 134—137).—A yield of over 70 per cent. of potassium chlorate is obtained when a neutral or slightly alkaline, 20 per cent. solution of potassium chloride, containing a small quantity of potassium dichromate is electrolysed with a current of 2 amperes, the temperature of the solution being maintained between 16° and 20°. If the solution is made more strongly alkaline, the yield of chlorate, and also of hypochlorite, is decreased, and if no potassium dichromate is present, the yield of potassium chlorate is never more than 35 per cent. (compare Foerster, *Zeit. Elektrochem.*, 1, 854).

H. R. LE S.

New Explosive and Detonating Materials. By UGO ALVISI (*Gazzetta*, 1899, 29, 478—490. Compare Abstr., 1899, ii, 414, 647, and 748).—The author gives the name *cremonites* to explosives composed of picric acid, or a picrate mixed with ammonium perchlorate. They keep well, require very powerful detonators, are more powerful than picric acid alone, and have a propulsive force nearly equal to that of the most powerful gelatin-dynamite.

Cannel powder is the name given to mixtures of coal and ammonium

perchlorate, 5 parts of the latter to 1 part of Scotch cannell giving the best results. It is simply prepared, has great resistance to shock, keeps well, is non-hygroscopic, and requires powerful detonators.

Ammonium perchlorate can be made on a commercial scale by the interaction of concentrated solutions of ammonium nitrate and sodium perchlorate.
T. H. P.

Crystalline Hydrates of Sodium Thiosulphate. By W. W. TAYLOR (*Proc. Roy. Soc. Edin.*, 1898, 22, 248—251).—Crystals of the composition $\text{Na}_2\text{S}_2\text{O}_3 + 2\text{H}_2\text{O}$ may be obtained by driving off part of the water from the fused pentahydrate and allowing the solution to cool. The solubility curves of the pentahydrate and dihydrate intersect at 50° , which is accordingly the transition temperature of the two hydrates. To obtain the dihydrate in quantity, anhydrous thiosulphate is dissolved in fused pentahydrate and the solution kept at 53° . Crystallisation is induced by adding a few fragments of dihydrate, and the crystals formed are dried in an oven at 53° .

J. C. P.

Preparation of Metallic Lithium. By LOUIS KAHLBERG (*J. Physical Chem.*, 1899, 3, 602—603).—Lithium may be obtained very readily by the electrolysis of solutions of lithium chloride in pyridine. A beaker with a concentrated solution of the salt in pyridine served as a cell, no diaphragm being used; a carbon pole was used as anode, and an iron plate as cathode; the E.M.F. was about 14 volts, the current density about 0.25 ampere per 100 sq. cm.; under these conditions, an adhering, silver-white deposit of metallic lithium was obtained.
L. M. J.

Action of Magnesium on Saline Solutions. By HENRI MOURAOUR (*Compt. rend.*, 1900, 130, 140—141. Compare Abstr., 1899, ii, 656).—A rapid evolution of hydrogen takes place when magnesium powder is added to cold solutions of ammonium chloride, ammonium carbonate, ammonium oxalate, ammonium sulphide, sodium carbonate, borax, common alum, and chrome alum. With solutions of sodium phosphate, sodium acetate, sodium nitrite, sodium thiosulphate, potassium sodium tartrate, potassium chloride, potassium ferrocyanide, barium chloride, calcium chloride, and strontium chloride, the evolution of hydrogen is slow, and with a solution of ammonium fluoride, hydrogen is not evolved.
H. R. LE S.

Metallic Borates. By LÉON OUVRARD (*Compt. rend.*, 1900, 130, 172—175).—The only well defined metallic salt of orthoboric acid is Ebelmen's magnesium borate, $\text{Mg}_3(\text{BO}_3)_2$ (*Ann. Chim. Phys.*, 1851, [iii], 33, 50). The evidence in support of the tribasic character of the acid is derived chiefly from the study of its esters.

Cadmium orthoborate, $\text{Cd}_3(\text{BO}_3)_2$, prepared by adding cadmium oxide (1 mol.) to a fused mixture of potassium hydrogen fluoride (1 mol.) and boric oxide (1 mol.), and treating the cooled product with water, separates in the form of prismatic needles not affected by water, but readily soluble in dilute acids. The crystals produce a

marked effect on polarised light, the plane of extinction being inclined at 9° to the principal axis. G. T. M.

Borates of Zinc, Manganese, Nickel, and Cobalt. By LÉON OUVREAU (*Compt. rend.*, 1900, 130, 335—338).—The compound, $3\text{ZnO} \cdot \text{B}_2\text{O}_3$, obtained by fusing zinc oxide with molecular proportions of potassium hydrogen fluoride and boric oxide, forms flat prisms which belong to the orthorhombic system and have a marked action on polarised light; they are decomposed by hot water and are readily soluble in dilute acids.

The following compounds were prepared in a similar manner: $3\text{MnO} \cdot \text{B}_2\text{O}_3$, from manganese chloride, carbonate, or precipitated borate, forms light-brown, transparent needles, which are not decomposed by hot water but are very soluble in dilute acids; $3\text{NiO} \cdot \text{B}_2\text{O}_3$, from nickel chloride, carbonate, or amorphous borate, forms short, clear, green prisms which are not attacked by hot water but are soluble in acids. In the case of cobalt, the borate obtained had the formula $2\text{CoO} \cdot \text{B}_2\text{O}_3$; if, however, less boric oxide is employed, then the compound $3\text{CoO} \cdot \text{B}_2\text{O}_3$ is obtained as rose-coloured, rhombic crystals.

H. R. LE S.

Behaviour of Zinc Oxide at High Temperatures. By ROBERT C. SCHÜPPHAUS (*J. Soc. Chem. Ind.*, 1899, 18, 987—989).—In heating a mixture of zinc oxide and carbon under pressure, a powder of a permanent canary-yellow hue was obtained; this when analysed shows a higher percentage of zinc than is contained in zinc oxide. Similar compounds may also be obtained by heating zinc oxide in a current of pure nitrogen, or in a vacuum, or with zinc dust under pressure. In each case, the product must be allowed to cool out of contact with the air. L. DE K.

Hydrolysis of Thallic Sulphate. By HUGH MARSHALL (*Proc. Roy. Soc. Edin.*, 1899, 22, 596—597).—A slightly acid solution of thallic sulphate gives a brown precipitate of hydroxide on dilution; the same precipitate is formed when the solution is warmed, probably owing to an increase of hydrolysis with temperature; ammonium sulphate seems to prevent the formation of the precipitate on warming, but it redissolves in any case on cooling. J. C. P.

New Micro-chemical Reactions of Copper. By Pozzi-Escot (*Compt. rend.*, 1900, 130, 90—91).—The iodide, $\text{CuI}_2 \cdot 4\text{NH}_3 \cdot \text{H}_2\text{O}$, is obtained in the form of small, blue tetrahedrons by adding ammonium iodide or sodium iodide to an ammoniacal solution of a cupric salt. An unstable compound, probably $\text{CuI}_4 \cdot 4\text{NH}_3$, is formed by adding ammonium iodide or sodium iodide to an ammoniacal solution of a cupric salt which is heated at 40° and contains sufficient ammonia to give a clear solution when hot. Under these conditions, the solution turns a yellowish-green colour, and deposits dark brown rhomboidal plates mixed with prismatic crystals of the same colour, and sometimes also with orange, orthorhombic plates. The colour and crystalline form of the deposit soon change, and after 10—40 minutes the deposit consists entirely of short, thick, flat prisms and triclinic

plates of a yellow colour and possessing a coppery lustre. When seen under the microscope, these changes are very characteristic.

H. R. LE S.

Action of Bromine on Copper Salts in Presence of Alkali Hydroxides. A New Test for Copper Salts. By DIOSCORIDE VITALI (*Chem. Centr.*, 1899, ii, 990—991; from *Boll. Chim. Farm.*, 38, 665—668).—When copper salts are treated with an alkali hydroxide in presence of an excess of bromine water, a brown to black precipitate of the peroxide CuO_2 is formed. Chlorine or iodine may be used instead of bromine, but the reaction then takes place much more slowly. The presence of 1/100000th part of copper in 1 c.c. of a solution of crystallised copper sulphate may be detected by the intense yellow coloration produced by evaporating the solution and treating the residue with potassium hydroxide solution and bromine water. By evaporating the solution to dryness, then adding a few drops of bromine water and again evaporating, a black residue of anhydrous copper bromide is left and by this method even 1/1000000th part of copper in 1 c.c. of a solution of the sulphate, may be detected. The black stain may be rendered more distinct by moistening the residue with concentrated sulphuric acid after evaporating with bromine water. By the action of alkali hydroxides and bromine on nickel and cobalt salts, the black hydroxides $\text{Ni}_2(\text{OH})_6$ and $\text{Co}_2(\text{OH})_6$ are formed. Platinum salts form the brown hydroxide $\text{PtO}_2(?)$. Manganese salts give a black and mercury salts a yellow precipitate. When bismuth oxide is treated with alkali and bromine water, the yellow hydroxide, $\text{Bi}(\text{OH})_3$, is first formed by the action of the alkali, and on heating is, by the action of the potassium hypobromite present, converted into a heavy brown powder of the oxide Bi_2O_4 . Lead salts behave in a similar manner, the yellow precipitate of lead oxybromide, which is first formed, being converted into the dioxide on heating; this oxide, unlike that of bismuth, is insoluble in a small quantity of dilute nitric acid.

E. W. W.

Action of Ammonia on Diammoniomeric Iodide. By MAURICE FRANÇOIS (*Compt. rend.*, 1900, 130, 332—335. Compare *Abstr.*, 1899, ii, 657).—When a solution of ammonia of sp. gr. 0.923 is added to mercuric iodide, white diammoniomeric iodide is first formed. This, on the further addition of a large excess of ammonia, is converted into ammoniodimercuric iodide. The latter change is limited and also reversible, for on the addition of a solution of ammonia containing a large proportion of ammonium iodide to ammoniodimercuric iodide, the latter is partly converted into diammoniomeric iodide.

H. R. LE S.

[**Luminosity of Mixtures of Thoria and Ceria.**] By HERMANN THIELE (*Ber.*, 1900, 33, 183—187).—The luminosity of mantles prepared from mixtures of thoria and ceria and heated in the Wehnelt arc (*Ann. Phys. Chem.*, 68, 260), is not appreciably changed by increasing the amount of ceria from 0—5 per cent., but with larger amounts the luminosity decreases owing to the increased resistance thereby caused.

In the flame of the Wehnelt arc, however, as with the Bunsen flame, the luminosity is a maximum with mixtures containing from 1—2 per cent. of ceria. W. A. D.

Separation of Gadolinite Earths and the Preparation of Pure Yttria. By WILHELM MUTHMANN and R. BÖHM (*Ber.*, 1900, 33, 42—49. Compare this vol., ii, 18).—The normal chromates of the rare earths are all more soluble than the corresponding sulphates. They have the general formula $M_2(\text{CrO}_4)_3 \cdot n\text{H}_2\text{O}$, and as a rule $n=8$. Separations of the rare earths may be more rapidly effected by the aid of these chromates than by any other known method, the separation being best accomplished by fractionally precipitating solutions of the readily soluble dichromates with potassium chromate. In the separation of yttria earths, it is essential that (1) both solutions must be extremely dilute; (2) the liquid must be kept in rapid ebullition during the precipitation; (3) the precipitate must be in an extremely finely divided state, and must be kept in intimate contact with the liquid. Minute directions are given in the original for securing these conditions. By employing this method, the authors have succeeded in obtaining pure yttria from commercial yttrium oxide after six fractionations, the last fraction consisting of pure yttrium chromate in the form of minute, deep red prisms.

The atomic weight of yttrium, determined from this fraction by conversion into sulphate and then igniting for 15—20 hours to convert into oxide, was found to be 88.97. Cleve (*Abstr.*, 1883, 292) gives 89.92.

The specific gravities of the earths from the six different fractions were found to be 6.06, 5.62, 5.43, 4.87, 4.83 (pure yttria), and that of the original mixture 5.62. Cleve and Höglund give 5.028, Nilson and Pettersson (*Compt. rend.*, 1880, 91, 232) give 5.06, and Ekeberg (*Phil. Mag.*, 14, 346) 4.842 for pure yttria.

The other constituents of the crude oxide are erbia, which yields olive-coloured octahedra with potassium chromate, and an earth which yields a chromate in the form of small, golden needles. J. J. S.

Gadolinium. By CARL BENEDICKS (*Zeit. anorg. Chem.*, 1900, 22, 393—421).—Gadolinium is separated from the other rare earths by crystallising the nitrates from nitric acid (*Abstr.*, 1896, ii, 475), and when a fairly pure nitrate is obtained, this is subjected to partial precipitation with dilute ammonia (*Abstr.*, 1891, 17). A determination of the atomic weight, by conversion of the oxide into sulphate, gave $\text{Gd} = 156.38$ (6 experiments: $\text{O} = 16$). The following compounds are described. Gadolinium oxide, Gd_2O_3 , is a white powder, easily soluble in acids, absorbs carbon dioxide from the air, is somewhat hygroscopic, and is not reduced by heating in a current of hydrogen. The *hydroxide* is a gelatinous precipitate, which rapidly absorbs carbon dioxide. The salts of gadolinium are mostly colourless, show no absorption spectrum, have a sweet, astringent taste, and are very similar to the salts of yttrium. The *chloride*, $\text{GdCl}_3 \cdot 6\text{H}_2\text{O}$, crystallises in thick, tabular, quadratic pyramids, and has a sp. gr. 2.424. The *bromide*, with $6\text{H}_2\text{O}$, crystallises in small,

pointed, rhombic tablets, of sp. gr. 2·844. The *platinichloride*, $\text{GdCl}_3 \cdot \text{PtCl}_4 + 10\text{H}_2\text{O}$, crystallises in orange-yellow, prismatic needles of sp. gr. 2·719. The *aurichloride* crystallises, with $10\text{H}_2\text{O}$, in yellow tablets of sp. gr. 2·706. *Gadolinium platinocyanide*, $2\text{Gd}(\text{CN})_3 \cdot 3\text{Pt}(\text{CN})_2 + 18\text{H}_2\text{O}$, obtained by the action of the sulphate on barium platinocyanide, crystallises in long, pointed, and tabular, red crystals of the rhombic system, having a green metallic lustre, and is isomorphous with the corresponding yttrium and erbium salts; sp. gr. 2·563. The *nitrate*, $\text{Gd}_3\text{NO}_3 + 6\frac{1}{2}\text{H}_2\text{O}$, separates over sulphuric acid, or by evaporation in the air, in large, triclinic crystals of sp. gr. 2·332. It also crystallises with $5\text{H}_2\text{O}$ from concentrated nitric acid in prisms of sp. gr. 2·406. The *double salt*, with ammonium nitrate, $\text{Gd}_3\text{NO}_3 \cdot 2\text{NH}_4\text{NO}_3$, crystallises in long, hair-like, deliquescent crystals. The *sulphate*, $\text{Gd}_2\text{SO}_4 + 8\text{H}_2\text{O}$, separates in small, lustrous, monoclinic crystals, and is isomorphous with yttrium sulphate; sp. gr. 3·007. The anhydrous salt has a sp. gr. 4·139. The *double salt*, with potassium sulphate, $\text{Gd}_2\text{SO}_4 \cdot \text{K}_2\text{SO}_4 + 2\text{H}_2\text{O}$, has a sp. gr. 3·503. 100 c.c. of a saturated potassium sulphate solution will hold 0·87—0·77 gram Gd_2O_3 in solution. The *selenate*, $\text{Gd}_2\text{SeO}_4 + 10\text{H}_2\text{O}$, crystallises at the ordinary temperature in large, colourless, rhombic prisms, is isomorphous with the yttrium and erbium selenates, and rapidly effloresces; sp. gr. 3·048. It separates, with $8\text{H}_2\text{O}$, at the temperature of the water-bath in nacreous crystals of sp. gr. 3·309. The anhydrous salt has a sp. gr. 4·175. The *double salt*, with potassium selenate, $\text{Gd}_2\text{SeO}_4 \cdot 3\text{K}_2\text{SeO}_4 + 4\text{H}_2\text{O}$, crystallises in slender, microscopic needles. *Gadolinium hydrogen selenite*, $\text{Gd}_2\text{SeO}_3 \cdot \text{H}_2\text{SeO}_3 + 6\text{H}_2\text{O}$, is an amorphous precipitate, which gradually forms aggregates of small needles. *Gadolinium ethyl sulphate*, $\text{Gd}_3\text{EtSO}_4 + 9\text{H}_2\text{O}$, obtained from the sulphate and barium ethyl sulphate, crystallises in large, transparent tablets belonging to the hexagonal system [$a : c = 1 : 0\cdot5014$], is stable in the air, effloresces over sulphuric acid, and, when heated at 115° , loses $3\text{EtOH} + 6\text{H}_2\text{O}$; sp. gr. = 1·923. The *vanadate*, $\text{Gd}_2\text{O}_3 \cdot 5\text{V}_2\text{O}_5 + 26\text{H}_2\text{O}$, crystallises in the triclinic system [$a : b : c = 1\cdot7083 : 1 : 0\cdot9894$; $\alpha = 84^\circ 51'$, $\beta = 94^\circ 51'$, $\gamma = 82^\circ 13\cdot5'$]. The *basic carbonate*, $\text{OH} \cdot \text{GdCO}_3 + \text{H}_2\text{O}$, obtained by treating the hydroxide with carbon dioxide, crystallises in small, microscopic needles. The *normal carbonate*, $\text{Gd}_2\text{CO}_3 + 13\text{H}_2\text{O}$ (?), is obtained by prolonged action of carbon dioxide on the hydroxide. The *oxalate*, with $10\text{H}_2\text{O}$, crystallises from concentrated nitric acid in large, monoclinic crystals; 1 gram of ammonium oxalate dissolved in 38 grams of water will hold 0·00083 gram of gadolinium oxide in solution. The *acetate* crystallises with $4\text{H}_2\text{O}$ in sparingly soluble, colourless, triclinic crystals of sp. gr. 1·611. The *propionate* crystallises in a vacuum desiccator in crusts of large, rhombic tufts. E. C. R.

Stable Hydrates of Manganese Chloride above 0° . By HARRY M. DAWSON and P. WILLIAMS (*Zeit. physikal. Chem.*, 1899, **31**, 59—68).—Investigation with the dilatometer shows that the ordinary hydrate of manganese chloride, $\text{MnCl}_2 + 4\text{H}_2\text{O}$, is transformed into the dihydrate at $57\cdot9^\circ$, at which temperature also the vapour tension of the dry tetrahydrate becomes equal to the vapour pressure of the saturated

solution; at the same temperature, there is a corresponding discontinuity in the solubility curve and in the density of the saturated solution. When a manganese chloride solution crystallises at about 70° , large, well-formed crystals are obtained which, after draining, washing with alcohol, and drying between filter paper, are found to have the composition $\text{MnCl}_2 + 2 \cdot 2\text{H}_2\text{O}$, confirming the dilatometer result. A better method of preparing the dihydrate is to pass hydrogen chloride into an alcoholic solution of manganese chloride saturated at the ordinary temperature; the crystals of the dihydrate which separate are pink, but deeper in tint than the ordinary tetrahydrate. The dihydrate is stable from 58 — 198° ; at the latter temperature, it is transformed into the anhydrous salt.

Marignac's β -tetrahydrate, obtained by crystallisation at 0 — 6° of a solution saturated at a higher temperature, represents a labile form at all temperatures. J. C. P.

Peroxides. By SIMEON M. TANATAR (*Ber.*, 1900, 33, 205—208).—Peroxides are usually divided into two classes, the members of one of which yield hydrogen peroxide on treatment with acids, whilst those of the other do not. Piccini (*Abstr.*, 1897, ii, 9) further states that the true (hydrogen peroxide yielding) peroxides reduce certain compounds, such as manganese dioxide, lead dioxide, and potassium permanganate, in presence of acids, and that they are never produced by oxidation carried out with nitric or hypochlorous acid.

The author suggests that the two classes of peroxides may not differ in chemical constitution, but that the differences between their reactions may be accounted for by thermochemical considerations. The heat developed by the action of acids on the "false" peroxides is less than that required for the formation of hydrogen peroxide. Nickel peroxide, which acts in most respects as a false peroxide, develops, however, sufficient heat to render possible the formation of hydrogen peroxide, and the author has found that perceptible amounts of hydrogen peroxide are actually produced by the decomposition of nickel peroxide with sulphuric acid. The peroxides of nickel and cobalt, moreover, appear capable of converting barium hydroxide into the peroxide, for in their presence barium hydroxide brings about the reduction of potassium permanganate. Potassium permanganate is also slowly decolorised in the cold when it is mixed with solutions of sodium hypochlorite and barium hydroxide. A. H.

Nature of the Change from Violet to Green in Solutions of Chromium Salts. By WILLIS R. WHITNEY (*J. Amer. Chem. Soc.*, 1899, 21, 1075—1084. Compare *Abstr.*, 1896, ii, 525).—The author considers that the conclusions of Venable and Miller (*Abstr.*, 1898, ii, 592) are erroneous, and describes experiments which confirm the observations of Recoura (*Abstr.*, 1896, ii, 27) and of Favre and Valson (*Compt. rend.*, 1872, 74, 1032). [Compare also Dougal (*Trans.*, 1896, 69, 1526.)] E. G.

A New Crystalline Molybdenum Sulphide. By MARCEL GUICHARD (*Compt. rend.*, 1900, 130, 137—140).—When molybdenum disulphide is heated in the electric furnace, it is decomposed, and a

new compound, *molybdenum sesquisulphide*, Mo_2S_3 , is formed; this crystallises in steel-grey needles of sp. gr. 5.9 at 15° . When slightly heated, it is readily decomposed by fluorine and chlorine, but only at a red heat by bromine, whilst iodine is without action on it, even at the higher temperature. When strongly heated in oxygen, molybdenum trioxide is formed, and in atmosphere of sulphur, it is converted into the disulphide. Hydrochloric and sulphuric acids have no action on it, but hot concentrated nitric acid and aqua regia readily dissolve it with formation of molybdic and sulphuric acids. If molybdenum sesquisulphide is heated to a temperature slightly higher than that at which it is formed, it is decomposed into metallic molybdenum, and, if carbon is present, the carbide CMo_2 is formed. H. R. LE S.

Enantiotropy of Tin. II. By ERNST COHEN and C. VAN ELJK (*Proc. K. Akad. Wetensch. Amsterdam*, 1899, 2, 149—153; *Zeit. physikal. Chem.*, 1899, 30, 601—622. Compare this vol., ii, 83).—The velocity of change of the white into the grey modification of tin has been determined, with the aid of a dilatometer, at various temperatures from 0° to -83° , and has a maximum at about -48° , which is accordingly the most favourable temperature for the conversion of white tin into grey tin.

Further qualitative investigation at a temperature of -4° to -7° shows that the change of dry white tin into grey tin takes place slowly, beginning at the edges. If the white tin has powdered grey tin in contact with it, the change is accelerated, and begins at the points of contact. White tin filings are much more rapidly converted than white block tin. J. C. P.

Enantiotropy of Tin. III. By ERNST COHEN (*Proc. K. Akad. Wetensch. Amsterdam*, 1899, 2, 281—286. Compare preceding abstract).—White tin can be inoculated with grey tin; a large block treated thus and kept at -5° for 3 weeks was photographed and seen to be covered with grey nodules.

Previous investigation has shown that the velocity of change of white tin into grey tin is a maximum at -40° , and zero at 20° . At the ordinary temperature, the velocity is small, and a very long time would be necessary for the transformation. This condition was regarded as fulfilled in the case of an antique vase dug up in Hampshire, and supposed to date from the fourth century; on examination, the vase was found to consist almost entirely of grey tin.

The velocity of the change of grey tin to white tin above 20° has been investigated with the aid of a dilatometer, and found to increase very rapidly, rendering measurement impossible at 40° . J. C. P.

Bismuth Suboxide and Subsulphide. By R. SCHNEIDER (*J. pr. Chem.*, 1899, [ii], 60, 524—543. Compare Abstr., 1899, ii, 227).—The following method for the preparation of bismuth suboxide, Bi_2O_3 , is simpler, and yields better results, than the two methods previously described by the author. A solution of bismuth oxide, Bi_2O_3 , in nitric acid, is poured slowly and with constant stirring into excess of dilute potassium hydroxide; the precipitate of bismuth hydroxide is washed by decantation, and then suspended in 2 per cent. potassium hydroxide in a

capacious flask; a solution of freshly prepared stannous chloride is slowly added, the flask completely filled with air-free water, tightly closed, and the contents well shaken. Bismuth suboxide is thus obtained as a light, perfectly homogeneous, black powder. If freely exposed to the air in a moist state, it is completely converted into ordinary bismuth hydroxide.

Bismuth subsulphide, Bi_2S_3 , is conveniently prepared by heating bismuth suboxide in a stream of dry hydrogen sulphide. It forms a slate-grey, dense, entirely homogeneous powder. When moderately heated in absence of air, it remains unchanged; at a low red heat, it melts and decomposes into bismuth and the ordinary bismuth sulphide. If heated in a current of hydrogen, it is reduced to the metal; the reduction begins at the temperature of melting sulphur, and then proceeds smoothly and rapidly.

The author replies in detail to the criticisms of Vanino and Treubert (*Abstr.*, 1899, ii, 428) on his previous communications, and adheres to his former conclusions. E. G.

Isomorphous Compounds of Gold and Mercury. By THEODOR H. BEHRENS (*Proc. K. Akad. Wetensch. Amsterdam*, 1899, 2, 163).—The halogen salts of these metals have been found to yield complete series of compound crystals. These were prepared by adding chlorides or bromides of thallium, caesium, and rubidium to mixed solutions of the chlorides and bromides of gold and mercury. J. C. P.

Preparation of Colloidal Metallic Solutions by the Disintegrating Action of an Electric Discharge. By GEORG BREDIG (*Zeit. angew. Chem.*, 1898, 951—954).—Hitherto colloidal metallic solutions have been obtained by the action of chemical reducing agents. The author describes how an electric discharge between poles of gold, silver, and platinum, immersed in water, disintegrates the cathode, and gives a solution of the metal. In the case of gold, reddish-purple or dark blue solutions are thus obtained, which can be filtered without change and keep their colour for months; the gold may be precipitated from the solution by freezing or by the addition of electrolytes; non-electrolytes, on the other hand, are ineffective. When the colloidal solution is subjected to electrolysis, the metal is separated at the anode as a black slime.

Silver and platinum give clear, dark brown solutions, which even with a small metal concentration absorb light almost entirely and are generally similar in properties to the colloidal gold solution. The colloidal platinum solution behaves like platinum black in decomposing hydrogen peroxide with evolution of oxygen.

Careful microscopic investigation reveals no heterogeneity, but the author is nevertheless of opinion that these solutions are really heterogeneous systems of the very finest structure, the particles having probably about a thousand times the molecular dimensions. The colours observed are regarded as due to this state of fine division. J. C. P.

Inorganic Ferments. I. Catalytic Action of Platinum, and the Chemical Dynamics of Hydrogen Peroxide. By GEORG BREDIG and R. MÜLLER VON BERNECK (*Zeit. Physikal. Chem.*, 1899, 31, 258—353).—Close analogy exists between the decomposition of

hydrogen peroxide by organic ferments (Jacobson, Abstr., 1892, 899), and by colloidal platinum. The latter agent is formed by the action of an electric discharge between platinum wires immersed in water, and the dark brown solution so obtained (with a maximum possible concentration of 1 gram-atom of platinum in 1300 litres of water) behaves in numerous cases exactly like platinum black. As this colloidal platinum is precipitated by electrolytes, its action is advantageously studied on hydrogen peroxide, which is practically a non-conductor, and yields non-electrolytic decomposition products.

Solutions of hydrogen peroxide were prepared with the conductivity 1.5×10^{-5} — 3.7×10^{-5} ; to a suitably diluted portion, some of the platinum solution was added, and the mixture was kept at a constant temperature (generally 25°); portions extracted from time to time were titrated with permanganate solution, and the progress of the decomposition of hydrogen peroxide thus determined. Even a solution of 1 gram-atom of platinum in about 70 million litres of water markedly accelerates the decomposition of hydrogen peroxide. The authors have compared with this the catalytic action of the peroxides of manganese, cobalt, copper, and lead, in both acid and alkaline solution.

The decomposition of hydrogen peroxide in acid and neutral solution in presence of colloidal platinum of constant quantity and condition, proceeds strictly according to the unimolecular equation, $2\text{H}_2\text{O}_2 = 2\text{H}_2\text{O} + \text{O}_2$. In alkaline solution, the catalytic action of colloidal platinum first increases, reaches a maximum, and then diminishes again, as the alkali concentration increases; this is exactly what happens in the action of organic ferments on hydrogen peroxide. The values for the velocity constant obtained in alkaline solution are not steady, probably owing to the partial combination of the hydrogen peroxide and the alkali, as indicated by freezing point and other experiments.

Colloidal platinum and organic ferments are both alike affected by the addition of electrolytes, but the analogy is perhaps most strikingly illustrated by the effect of certain poisons, such as hydrocyanic acid, hydrogen sulphide, and mercuric chloride; the colloidal platinum is, as it were, paralysed by these agents, but recovers itself after a certain time.

The catalytic action of the colloidal platinum solution increases with its concentration, although not proportionally, and is favoured by rise of temperature; the increase of the velocity constant in the latter case agrees well with Arrhenius' equation $\log_e k_1/k_2 = A(T_1 - T_2)/(T_1 \cdot T_2)$, where k_1 and k_2 are the velocity constants corresponding to the temperatures T_1 and T_2 , and A is a constant (Abstr., 1889, 1103). Light does not affect the catalytic action of the colloidal platinum.

The view that platinum acts on hydrogen peroxide as certain solids do on supersaturated gas solutions is not confirmed. The paper contains a review of various theories of catalytic action. J. C. P.

Platinum Tetrachloride. By ARTURO MIOLATI (*Zeit. anorg. Chem.*, 1900, 22, 445—465).—The electric conductivity of aqueous solutions of platinum tetrachloride is not constant, but alters with the

time, and the values are dependent on the dilution; the results are essentially those given by a weak acid, and are similar to those obtained with selenious acid. An aqueous solution of platinum tetrachloride, when titrated with sodium hydroxide, using phenolphthalein as indicator, is neutralised with two equivalents of alkali; and by determining the specific conductivity of solutions to which successive quantities of alkali are added, unmistakable evidence of the formation of an acid and a normal salt is obtained. This is more clearly shown when ammonia is used to neutralise the solution. It is therefore evident that a solution of platinum tetrachloride contains a dibasic acid. The silver salt, $\text{Ag}_2\text{PtCl}_4(\text{OH})_2$, has been known for some time. The author was unable to isolate the alkali salts from their solution. Copper, zinc, or cadmium hydroxides dissolve in the aqueous solution, but the resulting salts do not crystallise, and yellowish-brown gums are obtained, easily soluble in water and alcohol. The alcoholic solution, when precipitated with ether, yields yellow, gummy flocks, which solidify after a time, and these, on analysis, gave numbers agreeing fairly well with the formulæ $\text{ZnPtCl}_4(\text{OH})_2 + 3\text{H}_2\text{O}$ and $\text{CdPtCl}_4(\text{OH})_2$. The *thallium* salt, $\text{Tl}_3\text{Pt}_2\text{Cl}_8\text{H}_5\text{O}_4$, obtained by precipitating an aqueous solution of the tetrachloride with a thallium salt, is a yellow, amorphous powder. The *lead* salt, $\text{PbPtCl}_4(\text{OH})_2$, is obtained as a yellow precipitate by adding a mixture of lead and sodium acetates to the aqueous solution; the *lead* salt, $\text{PbPtCl}_4(\text{OH})_2, \text{Pb}(\text{OH})_2$, obtained in alcoholic solutions, is a brownish powder. E. C. R.

Nature of Palladium Hydrogen. By JOHN SHIELDS (*Proc. Roy. Soc. Edin.*, 1898, 22, 169—186).—The E.M.F. of the combination—palladium containing a small quantity of hydrogen | dilute sulphuric acid | palladium containing a large quantity of hydrogen—is zero, or nearly so. Thus the cell does not behave like a true concentration cell, as would probably be the case were the absorption of hydrogen by palladium simply a process of solution. The view that a chemical compound is formed would agree better with the facts, for the E.M.F. in this case would be independent of the quantity of compound formed. The experiments are insufficient to determine whether the compound formed is Pd_3H_2 , or whether it contains more hydrogen than corresponds with this formula. J. C. P.

Mineralogical Chemistry.

Accumulation of Iron in Peat. By JACOBUS M. VAN BEMMELEN [with C. HOITSEMA and EDUARD A. KLOBBIE] (*Zeit. anorg. Chem.*, 1899, **22**, 313—379).—This paper covers, but in greater detail, much the same ground as one already noticed (*Abstr.*, 1899, ii, 371). Several more analyses of impure chalybite, iron ochre and vivianite are given.

L. J. S.

Formation of Petroleum. By CARL ENGLER (*Ber.*, 1900, 33 7—21).—Krämer and Spilker's arguments (this vol., i, 73) are inconclusive, and their experiments were hardly needed, for the author had shown already that all fats and waxes, whether of animal or vegetable origin, yield petroleum when distilled under pressure. He explains at some length his view of the mode of formation of petroleum. This was, he thinks, formed in the main by the decomposition of animal deposits of marine origin; the nitrogenous matter in this decomposed comparatively rapidly, leaving a wax almost free from nitrogen; this became buried under subsequent deposits, and was in consequence subjected to greater pressure and a higher temperature, under the influence of which it yielded petroleum. C. F. B.

Graftonite, a new Mineral. By SAMUEL L. PENFIELD (*Amer. J. Sci.*, 1900, [iv], 9, 20—32).—The new mineral is found associated with beryl, tourmaline, &c. in pegmatite on Melvin Mountain, near Grafton, New Hampshire. The fragments and indistinct crystals have a rough, weathered appearance, and are striking in being built up of thin, alternately light and dark lamellæ, the light material being graftonite and the dark oxidised triphylite; in a fresh specimen, the two minerals are salmon-coloured and pale green respectively. The graftonite has a vitreous to resinous lustre and closely resembles salmon-coloured lithiophilite in appearance. Analyses of the separated minerals are given under I (grafftonite, sp. gr. 3·672) and II (triphylite, Li(Fe,Mn)PO_4 , sp. gr. 3·58); analysis III, by W. E. Ford, was made on partly oxidised graftonite imperfectly separated from triphylite. Details of the method of analysis are given.

	P_2O_5	FeO.	MnO.	Fe_2O_3	CaO.	MgO.	K_2O	Na_2O	Li_2O	H_2O	Total.
I.	41·20	30·65	17·62	—	9·23	0·40	—	—	0·33	0·75	100·18
II.	42·3	33·4	9·9	—	0·2	1·3	—	—	9·2	1·7	98·0
III.	40·80	24·28	15·38	10·16	7·25	—	0·14	1·15	—	1·17	100·33

These analyses (in III calculating the whole of the iron as ferrous) give the formula for graftonite as $(\text{Fe,Mn,Ca})_3\text{P}_2\text{O}_8$ or $\text{R}''_3\text{P}_2\text{O}_8$. Few other anhydrous, normal phosphates are known amongst minerals. Crystals of graftonite are monoclinic with approximately $a:b:c = 0·886:1:0·582$; $\beta = 66^\circ$. The peculiar intergrowth of the monoclinic graftonite and the orthorhombic triphylite is discussed in detail; there appears to be a definite crystallographic relation between the two minerals. Similar cases are the intergrowth of albite and orthoclase, rutile and hæmatite. L. J. S.

Anhydrite and Gypsum Deposits at Oulx, Piedmont. By LUIGI COLOMBA (*Jahrb. f. Min.*, 1900, i, Ref. 26—28; from *Atti Accad. Sci. Torino*, 1898, 33, 779—796).—The deposits of gypsum and anhydrite near Oulx, in an upper valley of the Dora Riparia, occur with beds of limestone, sometimes dolomitic, from which, it is suggested, the calcium sulphate has been derived by the action of volcanic gases. A description is given of each of the following minerals which occur in both the limestone and the gypsum: mica, tourmaline, quartz, chalcedony, pyrites, sulphur, dolomite, halite, hæmatite and blende.

The optically uniaxial mica occurs as minute scales, and is shown

by the following analysis to be a biotite containing lithium ; it differs from ordinary lithia mica in containing much magnesia.

SiO ₂ .	Al ₂ O ₃ .	MgO.	CaO.	Li ₂ O.	Na ₂ O, (K ₂ O).	Loss on ignition (H ₂ O, F).	Total.
42.40	12.66	20.10	6.76	5.21	4.68	6.82	98.63

Analysis of the dolomite gave MgCO₃, 42.75 ; CaCO₃, 57.21 = 99.96.
L. J. S.

[Celestite from Baltschiederthal, Switzerland.] By CARL SCHMIDT (*Jahrb. f. Min.*, 1900, i, 16—21).—The fissured masses of Triassic dolomitic limestone folded in the gneisses of the Baltschiederthal, Wallis, contain in the crevices, crystals of dolomite, celestite, fluor, calcite, quartz, barytes, adularia, anatase, blende, &c. A description is given of each of these minerals. Bluish crystals of celestite gave the following results on analysis by M. Scheid :

SrO.	BaO.	CaO.	SO ₃ .	SiO ₂ , Al ₂ O ₃ , Fe ₂ O ₃ .
54.29	0.25	0.17	42.72	traces

L. J. S.

[Mineral Analyses.] By KARL BUSZ (*Jahrb. f. Min.*, 1899, *Beil. Bd.*, 13, 90—139).—In a petrological paper describing the granite and contact rocks of the Dartmoor Forest, Devonshire, the following analyses are given of minerals from the metamorphosed Devonian limestone at South Brent.

Garnet occurs abundantly, in one case as a vein two metres wide ; the brownish-green, rhombic dodecahedra and granular masses show marked optical anomalies ; Analysis I (contains also traces of manganese, magnesium and sodium) shows the mineral to be andradite with the formula $9(\text{Ca}_3\text{Fe}_2\text{Si}_3\text{O}_{12}) + \text{Ca}_3\text{Al}_2\text{Si}_3\text{O}_{12}$.

Datolite occurs as a white, saccharoidal mass in which the garnets are embedded ; anal. II (B₂O₃ by difference 21.65 ; also a trace of sodium). This is a very unusual mode of occurrence of datolite.

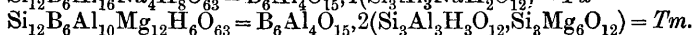
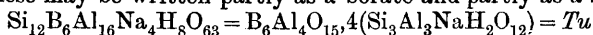
Augite occurs in large, grey-green masses which are fibrous or compact : Analysis III shows it to be hedenbergite ; the ferric oxide is due to oxidation, as the mineral is not quite fresh.

	SiO ₂ .	Al ₂ O ₃ .	Fe ₂ O ₃ .	FeO.	MnO.	CaO.	MgO.	K ₂ O.	H ₂ O.	Total.	Sp. gr
I.	37.17	2.80	26.93	Nil	—	32.34	—	0.58	0.65	100.47	3.65
II.	36.10	1.68		—	—	34.55	—	trace	6.02	—	2.76
III.	49.29	0.29	4.92	16.70	0.86	22.55	5.49	—	—	100.10	—

Other secondary minerals present in the limestone are axinite and quartz.
L. J. S.

Theory of Tourmaline Mixtures. By GUSTAV TSCHERMAK (*Tsch. Min. Mitth.*, 1899, 19, 155—164. Compare Abstr., 1899, ii, 304, 601, 767).—From a consideration of Riggs's analyses (Abstr., 1888, 659), Wülfing showed (Abstr., 1889, 765) that tourmalines may be considered to be isomorphous mixtures of the two silicates, Si₁₂B₆Al₁₆Na₄H₆O₆₂ and Si₁₂B₆Al₁₀Mg₁₂H₆O₆₃, in which aluminium may

be replaced by iron, and magnesium by iron, calcium, &c. Each of these may be written partly as a borate and partly as a silicate :



These formulæ, the silicate portions of which represent paragonite and merxene respectively, express the relations existing between the micas and tourmalines as shown by their modes of origin, occurrence, alteration, &c. The relation is similar to that shown by the author to exist between the plagioclase and scapolite groups. Most tourmaline analyses can be explained by mixtures of the above molecules ; for example, Penfield and Foote's recent analyses (Abstr., 1899, ii, 304) give $Tu_{44}Tm_7$ (Haddam Neck), and $Tu_{13}Tm_{37}$ (De Kalb). A few analyses are explained by the presence of a third molecule :

$\text{Si}_{12}\text{B}_6\text{Al}_8\text{Mg}_{12}\text{H}_8\text{O}_{61} = \text{B}_6\text{Al}_4\text{O}_{15}, 2(\text{Si}_3\text{Al}_2\text{H}_4\text{O}_{11}), \text{Si}_3\text{Mg}_6\text{O}_{12} = Tn$, of which the silicate portion has the phlogopite formula. L. J. S.

Kelyphite. By JOSEF MRHA (*Tsch. Min. Mitth.*, 1899, 19, 111—143).—A microscopical examination of the fibrous shells of kelyphite surrounding garnets in serpentine shows the material to consist of a mixture of augite, spinel, bronzite and hornblende. The composition of the kelyphite from near Steinegg, Austria, is given under I, and the spinel (picotite), isolated from it, gave II. The garnet (pyrope) gave III. The alteration of olivine and pyrope to augite and spinel is accompanied by an increase in molecular volume.

	SiO ₂ .	Al ₂ O ₃ .	Cr ₂ O ₃ .	Fe ₂ O ₃ .	FeO.	MnO.	CaO.	MgO.	Loss on ignition.	Total.	Sp. gr.
I.	41·12	15·38	2·63	4·18	4·01	0·39	4·73	25·54	0·92	98·90	—
II.	—	51·34	12·40	6·88	9·36	—	—	19·88	—	99·86	3·726
III.	42·29	21·12	2·86	8·11		0·36	5·42	19·90	—	100·06	3·697

L. J. S.

[Allophane from Italy.] By GIOVANNI D'ACHIARDI (*Jahrb. f. Min.*, 1900, i, Ref. 16, 29 ; from *Proc. Verb. Soc. Toscana Sci. Nat.*, 1898, 12, 26—39).—Sky-blue to grey-blue, optically isotropic allophane fills crevices and forms reniform crusts in zinc ores at Valdaspra, Massa Maritima, Tuscany, where it is associated with linarite, aurichalcite (Abstr., 1898, ii, 604), &c. After deducting zinc, copper and calcium as hemimorphite, chrysocolla and calcite, analysis I gives the formula $\text{Al}_2(\text{OH})_2\text{SiO}_4 + 5\text{H}_2\text{O}$.

Allophane from Rosas, Sulcis, Sardinia, gave II (also contains Cr_2O_3 , trace) from which, after deducting excess of silica as hyalite, the formula is deduced as $\text{Al}_2(\text{OH})_2\text{SiO}_4 + 4\text{H}_2\text{O}$.

	SiO ₂ .	Al ₂ O ₃ .	ZnO.	CuO.	CaO.	H ₂ O, (below 350°).	H ₂ O, ignition.	Total.	Sp. gr.
I.	24·00	32·01	1·44	1·21	0·66	32·90	6·49	98·72	1·93
II.	30·39	32·63	1·63	1·18	0·23	27·18	5·88	99·12	2·00—2·086

Cupriferous allophane is also described from a copper mine at Cascine, Mezzanago ; it contains no zinc and only a trace of calcium.

L. J. S.

New Occurrence of Laumontite. By OTTO LUEDECKE (*Zeit. f. Naturwiss.*, 1899, 72, 101—104).—The quartz-porphry on Peters-

berg, near Halle, contains embedded laumontite, associated with secondary fluorite, calcite, epidote and quartz. The laumontite has been apparently derived from oligoclase; it is reddish-yellow, and without crystal faces. The mean of two analyses is, after deducting a little calcite,

SiO ₂ .	Al ₂ O ₃ .	CaO.	H ₂ O.	Total.
50·66	22·26	13·60	13·56	100·09

L. J. S.

Action of Ammonium Chloride on Analcite and Leucite. By FRANK W. CLARKE and GEORGE STREIGER (*Amer. J. Sci.*, 1900, [iv], 9, 117—124; and *Zeit. anorg. Chem.*, 1900, 23, 135—145).—In a previous paper (this vol., ii, 25), it was shown that analcite, when heated at 350° in an open crucible with ammonium chloride, gave up part of its soda and absorbed some ammonia; at a higher temperature, ammonia is again liberated. Further experiments have now been made on analcite from North Table Mountain, near Golden, Colorado, the composition of which is given under I. When the material is heated at 350° in a sealed tube with ammonium chloride, the whole of the soda is converted into sodium chloride, and all the liberated ammonia absorbed by the silicate; the residue has the composition $\text{NH}_4\text{AlSi}_2\text{O}_6$, and appears to be the first ammonium silicate that has been prepared. In the presence of excess of free ammonia there is no further absorption of ammonia. On boiling this ammonium compound with caustic soda solution, the whole of the ammonia is expelled and sodium again taken up. The product previously obtained with analcite is now to be regarded as a mixture.

Leucite (from Vesuvius, anal. II.), when heated in a sealed tube with ammonium chloride, yields the same compound, $\text{NH}_4\text{AlSi}_2\text{O}_6$, as does analcite. When this ammonium leucite, the composition of which is given under III, is fused with calcium chloride, a product approximating in composition to the corresponding calcium salt, $\text{CaAl}_2\text{Si}_4\text{O}_{12}$, is obtained. This ammonium leucite is not a metasilicate, as shown by the fact that no soluble silica is liberated when the material is ignited.

	SiO ₂ .	Al ₂ O ₃ .	CaO.	K ₂ O.	Na ₂ O.	H ₂ O.	NH ₃ .	Total.
I.	55·72	23·06	0·17	—	12·46	8·39	—	99·80
II.	55·40	23·69	0·16	19·54	1·25	0·24	—	100·28
III.	60·63	26·44	trace	0·50	0·25	5·17	7·35	100·34

Preliminary experiments show that several other zeolites behave in a similar manner when heated with ammonium chloride.

L. J. S.

Granitoid Rocks from Cape Marsa. By LOUIS DUPARC and F PEARCE (*Compt. rend.*, 1900, 130, 432—434).—Petrographical descriptions, with analyses, are given of granulite, tonalite and microtonalite.

L. J. S.

Eruptive Rocks from the Salzkammergut. By CONRAD H. VON JOHN (*Jahrb. k.k. geol. Reichs. Wien*, 1899, 49, 247—258).—Quartz-diorite (=tonalite) from the Pöllagraben, St. Gilgen, consisting of plagioclase, hornblende and biotite with some orthoclase and

quartz, gave analysis I; the large crystals of white felspar (andesine) isolated from the rock gave II.

	SiO ₂ .	TiO ₂ .	Al ₂ O ₃ .	Fe ₂ O ₃ .	FeO.	CaO.	MgO.	K ₂ O.	Na ₂ O.	P ₂ O ₅ .	Loss on ignition.	Total.
I.	58.20	0.21	19.20	2.01	4.42	5.60	3.25	1.81	4.53	0.33	1.28	100.84
II.	58.97	—	25.21	0.65	—	6.82	0.21	0.71	6.02	—	0.50	99.09

Analyses of several other rocks are given.

L. J. S.

Analyses of Italian Volcanic Rocks. II. By HENRY S. WASHINGTON (*Amer. J. Sci.*, 1900, [iv], 9, 44—54. Compare this vol., ii, 27).—Six analyses are given of various volcanic rocks from Tuscany and Rome.

L. J. S.

Plagioliparites of Cape Marsa, Algeria. By LOUIS DUPARC and F. PEARCE (*Compt. rend.*, 1900, 130, 56—58).—The plagioliparites of Cape Marsa, in Algeria, consist of plagioclase, biotite and quartz in a matrix which may be vitreous, globular, felsitic or perlitic with large spheruliths, but in all cases the composition is practically the same: SiO₂, 72.74—77.99; Al₂O₃, 12.46—12.70; Fe₂O₃, 1.06—1.91; CaO, 1.21—1.59; MgO, 0.05—0.15; K₂O, 4.10—5.71; Na₂O, 2.85—3.60; loss on heating, 0.24—2.92 per cent.

C. H. B.

Meteorites from Jamyscheff and Tubil River, Siberia. By J. A. ANTIPOFF (*Chem. Centr.*, 1899, i, 801; from *Bull. Acad. St. Pétersbourg*, 1898, [v], 9, 91—103).—Analysis I is of the metallic portion of the meteorite which fell in the neighbourhood of the village of Jamyscheff, Pawlodarsk district in Semipalatinsk (it contains also graphite, 0.115; howardite, 0.595; magnetite, 2.284; Cr, trace); the olivine gave the results under II, agreeing with the formula (Mg,Fe)₃SiO₈.

Analysis III is of the meteoric iron found on the Tubil river, Ats-hinsk district, Gov. Yeniseisk.

	Fe.	Ni.	Co.	SiO ₂ .	Ca.	Mn.	Mg.	As.
I.	86.634	7.985	0.603	0.160	0.392	—	0.057	trace
III.	95.183	3.385	0.140	0.075	0.205	0.090	0.033	0.019

	Cl.	C.	O.	S.	CO ₂ .	H ₂ O.	Schreibersite.	Total.
I.	0.120	0.071	0.509	0.012	0.047	0.144	0.366	100.094
III.	0.038	0.120	0.093	—	—	—	0.425	99.806

	SiO ₂ .	FeO.	Al ₂ O ₃ .	MgO.	MnO.	SnO ₂ .	Total.
II.	39.80	16.34	0.27	43.68	trace	trace	100.11

L. J. S.

Waters of the Salt Lake of Urmi, Persia. By R. T. GUNTHER and J. J. MANLEY (*Proc. Roy. Soc.*, 1899, 65, 312—318).—The water has the specific gravity 1.113 at 15° and contains about 15 per cent. of solid matter; of this, 86 per cent. is estimated to be sodium chloride, the rest consisting of magnesium chloride, magnesium sulphate, calcium sulphate, and potassium sulphate. No iodide or bromide can be detected.

J. C. P.

Physiological Chemistry.

Action of certain Derivatives of Morphine on Respiration in Man. By HUGO WINTERNITZ (*Chem. Centr.*, 1899, ii, 884—885, from *Therap. Monatsh. Sept.*).—Whilst the alkyl-morphine derivatives codeine and dionine hardly affect respiration, the acetyl derivatives, diacetylmorphine and monoacetylmorphine exacerbate breathing by stimulation of the respiratory centre. The action of morphine on respiration is thus weakened by the introduction of alkyl radicles, and increased by that of acetyl. W. D. H.

Action of the Constant Current on the Respiration of 'Surviving' Muscle. By TH. GUILLOZ (*Compt. rend.*, 1900, 130, 200—203).—In view of the treatment of maladies of nutrition (gout, obesity) with the constant current, advocated by the author, experiments on the respiration of the excised muscles of the frog were undertaken: the evolution of carbon dioxide and using up of oxygen were found to be increased during and after the use of the electrical stimulation. W. D. H.

Carbonic Oxide in Tobacco Smoke. By FRITZ WAHL (*Pflüger's Archiv*, 1899, 78, 262—285).—The carbonic oxide in tobacco smoke is taken up by the blood, but when highly diluted in this way, the gas may be breathed for 4 hours without ill results. W. D. H.

The Supposed Oxidation of Carbonic Oxide in the Living Body. By JOHN SCOTT HALDANE (*J. Physiol.*, 1900, 25, 225—229).—Wachholtz and Saint Martin have stated that carbonic oxide is converted into carbon dioxide in the body. The present experiments on mice entirely negative this. W. D. H.

The Influence of Animal Membrane on the Diffusion of Various Substances. By SVEN G. HEDIN (*Pflüger's Archiv*, 1899, 78, 205—261).—The diffusion of a large number of organic and inorganic substances was investigated with and without a membrane. The membrane used was prepared from the intestine; previous heating of the membrane makes no difference to the dialysis quotient. In all cases, the presence of a membrane hinders diffusion, but to an unequal extent. Taking dextrose as a standard, it was found that mannitol, erythritol, glycerol, glycocine, and alanine were hindered to the same extent as dextrose. The dialysis of some substances, such as alcohol, urea, urethane, and ethylene glycol, was less hindered than that of dextrose. The same is true for many neutral salts of the alkalis and alkaline earths; here the dissociation of the salts in solution forms one of the determining factors. Ammonium salts with two ions have often a greater dialysis quotient than the equally dissociated salts of the fixed alkalis, but ammonium sulphate behaved like the sulphates of the fixed alkalis. W. D. H.

Pressure Filtration of Proteids. By DAVID FRASER HARRIS (*J. Physiol.*, 1900, 25, 207—211).—The following proteids pass under pressure through a Chamberland filter: egg-albumin, serum-globulin (from sheep), serum-albumin, gelatin, acid-albumin, alkali-albumin, hæmoglobin, proteose, lactalbumin, caseinogen dissolved in alkali (1 to 30 per cent. of sodium hydroxide). The following do not: caseinogen of normal milk, caseinogen of decalcified or oxalated milk, caseinogen dissolved in lime-water, serum-globulin (from ox). The assumption drawn is that caseinogen in milk is particulate, or that its molecules are larger than those of the other proteids examined.

W. D. H.

Metabolism of a Vegetarian. By THEODOR RUMPF and O. SCHLUMM (*Zeit. Biol.*, 1899, 39, 153—158).—Particulars of the diet and excreta of the young vegetarian under observation are given. He took purely vegetable food, and presented nothing noteworthy in general health, weight, or appearance. His fæces, however, were extraordinarily voluminous. He took daily 11·82 grams of nitrogen, 698·21 grams of carbohydrate, and 28·64 grams of fat, and excreted daily 6·91 grams of nitrogen in his urine, and 4·01 in fæces; the fæces contained 7·58 grams of fat.

W. D. H.

Metabolism in Children. By WILLIAM CAMERER and FRIEDRICH SÖLDNER (*Zeit. Biol.*, 1899, 39, 37—72).—The observations first recorded were made on a girl thirty-nine weeks old, taking mixed diet. The results are given in tables, showing the composition of the diet, the growth of the child, and the composition of the excreta, including sweat. The second set of observations were similar ones upon twins; their nutriment was mother's milk. The presence of soaps in human milk is noted. The methods used are described in detail.

W. D. H.

Metabolism in Ruminants. By OSKAR HAGEMANN (*Chem. Centr.*, 1899, ii, 1030; from *Arch. Anat. Physiol.*, 1899, Suppl., 111—140 and 382).—If the oxygen used is taken as a measure of the energy that results, the sheep is much under the average values, and this is also lower than the digestive value. After the taking of food, the oxygen used increases by 5·5 per cent., which is a proof of anabolic processes that are furthered by digestion. Calorimetrically, a food of the value of 3705 Cal. is accompanied with an output of 1487 Cal., and proteid built up, 8 Cal.; this leaves 2210 Cal. for fat deposition and the needs of respiration. In the second paper, some of these figures are corrected; the figures relate only to the 8 or 10 hours following digestion, and the figure 2210 must be lessened to 1983 Cals. in order to allow for the methane that leaves the body.

W. D. H.

Metabolism of Phosphorus. By DIARMID NOËL PATON, J. CRAUFURD DUNLOP, and R. S. AITCHISON (*J. Physiol.*, 1900, 25, 212—224).—In dogs on a vegetable diet, much of the phosphorus in the food is not excreted in the urine; also a large proportion of phosphoric acid subcutaneously injected as sodium phosphate does not reappear in the urine; in the goat, none reappears, whether it is given in the food or injected under the skin. During lactation in the goat, the excretion

of phosphorus by the bowel is diminished, but under other circumstances, with the animal in phosphorus equilibrium, the absorption and excretion of phosphorus by the intestine are equal. In the dog, during lactation, the phosphorus in the urine is diminished. Goat's milk contains a high proportion of phosphorus, but less of it is in organic combination than in cow's or human milk. The administration of calcium glycerophosphate causes no rise in the phosphorus of the urine of the dog, or in the urine or milk of the goat. W. D. H.

Metabolism with Edestin. By RICHARD LEIPZIGER (*Pflüger's Archiv*, 1899, 78, 402—422).—Steinitz (Abstr., 1898, ii, 615) showed that feeding with proteids containing phosphorus yields better results so far as the putting on of phosphorus is concerned than feeding with phosphorus-free proteids *plus* inorganic phosphates. It was considered desirable to repeat this. Edestin was used instead of the myosin employed by Steinitz. The experiments were made on dogs, and Steinitz's results are confirmed. Another point investigated was the metabolic processes in which calcium and magnesium are concerned. Two experiments are recorded; in both there was a laying on of calcium in the body; in one there was a small gain, in the other a small loss, of magnesium. The results cannot be alone explained on the supposition of metabolic processes taking place in the bony tissues. W. D. H.

Metabolism during Poisoning by Pulegone. By W. LINDEMANN (*Zeit. Biol.*, 1899, 39, 1—17).—Substances which produce fatty degeneration, such as phosphorus, chloroform, and many other less thoroughly investigated materials, cause also a destructive metabolism of proteid. Pulegone, the active constituent of the ethereal oil of *Mentha pulegium*, is one of these. The substance was given subcutaneously to dogs. It causes great fatty degeneration of liver, kidneys, and heart, with hyperæmia and ulcerations of the intestines and other parts. The metabolic phenomena during the poisoning were investigated in the usual way by examining the ingesta and excreta, including the expired air. Proteid katabolism is much increased. The figures given support Voit's view that the fat originates from proteid. W. D. H.

Absorption and Excretion of Iron. By EMIL ABDERHALDEN (*Zeit. Biol.*, 1899, 39, 113—152).—This is a contribution to a much discussed question. In the main the methods (microchemical, &c.) are like those employed by others. The animals chiefly used were rats. The principal results are that inorganic iron given by the mouth as ferric chloride is absorbed in small doses. The iron of hæmoglobin and hæmatin is also absorbable. The duodenum is the principal seat of absorption; probably Peyer's patches are also seats of absorption. Iron is excreted in cæcum, colon, and rectum. The most trustworthy method of detecting iron is by ammonium sulphide and ammonia. W. D. H.

Absorption of Sugars in the Intestine. By E. HEDON (*Compt. rend.*, 1900, 130, 265—266).—The absorption of sugars in the intestine is related to their osmotic pressures. It is greatest for the two

hexoses studied (dextrose and galactose), less for arabinose, and very feeble in the case of raffinose. W. D. H.

Digestion of Starch in the Stomach of Carnivora. By HANS FRIEDENTHAL (*Chem. Centr.*, 1899, ii, 1030; from *Arch. Anat. Physiol.*, 1899, Suppl., 383—390).—Although the saliva of dogs contains no ptyalin, energetic digestion of starchy food occurs in their stomachs. This is not due to a zymogen in the swallowed saliva being rendered active when it reaches the stomach, for it occurred also in the stomach of an animal fed by an œsophageal fistula, in which no saliva was allowed to enter the stomach. The starch is changed into erythrodextrin; only quite small quantities of maltose were found.

W. D. H.

Relative Digestibility of Certain Fats in the Human Intestine. III. Butter and Margarine. By H. LÜHRIG (*Chem. Centr.*, 1899, ii, 1029—1030; from *Zeit. unters. Genussm.*, 2, 769—783).—The digestibility of margarine is given as 96·75; that of butter from 96·86 to 97·13 per cent. These numbers are rather higher than those of Hultgren and Landergren. Ox-fat appears to diminish digestibility. In estimating the fat of the fæces, allowance is made for lecithin and unsaponifiable substance.

W. D. H.

Nutritive Value of Margarine compared with Butter. By E. BERTARELLI (*Exper. Stat. Rec.*, 1899, 11, 375—376; from *Riv. Ig. San. Pubbl.*, 1898, 9, 538—545 and 570—579).—The results of experiments with men showed that margarine, when properly prepared, does not differ much from butter in chemical and physical properties. When margarine was consumed, 93·5 to 96 per cent. of fat was assimilated; with butter, 94 to 96 per cent. There was no disturbance of the digestive tract when margarine was consumed in moderate amounts.

N. H. J. M.

Effects of Thyroid Feeding on Monkeys By WALTER EDMUNDS (*Proc. Roy. Soc.*, 1899, 65, 368—369).—The effect of feeding monkeys on powdered thyroid, or Hutchison's thyrocolloid, in doses varying from the equivalent of one-half to that of three sheep's thyroids daily, is exophthalmos, wasting, weakness, and death. Other symptoms noted were erection of the hair on the head, falling off of hair in patches in other parts, and paralysis of one or more limbs. Some of these are due to stimulation of the cervical sympathetic nerve. The increased secretion of the enlarged and altered thyroid in Graves's disease probably explains the exophthalmos there.

W. D. H.

The Thyroid as a Poison-removing Organ. By FRITZ BLUM (*Virchow's Archiv*, 1899, 158, 495—513. Compare Abstr., 1899, ii, 125, 779).—This is a re-statement of the author's views on the functions of the thyroid.

W. D. H.

Defence of the Organism against the Toxic Properties of Glandular Secretions. By ALBERT CHARRIN and LEVADITI (*Compt. rend.*, 1900, 130, 262—264).—If digestion juices, especially pancreatic juice, are introduced into the tissues, injury occurs. In

the intestine, it is harmless. The protection is considered to be due to the action of the mucous membrane (removal of which leads to loss of protection), of intestinal parasites, and perhaps of the blood. In the upper part of the intestine, this is believed to be aided by the layer of mucus, and the glandular secretions from the wall of the intestine.

W. D. H.

Physiology of the Suprarenal Capsules. By H. BORUTTAU (*Pflüger's Archiv*, 1899, **73**, 97—128).—The paper is mainly a review of previous work on the subject; some points are amplified. The suprarenals are considered to have nothing to do with blood and skin pigments; their chief use is to render harmless the products of muscular activity, and so to regulate the nutrition and innervation of the whole motor apparatus.

W. D. H.

Influence of Alcohol on Milk Formation. By RUDOLF ROSE-MANN (*Pflüger's Archiv*, 1900, **73**, 466—504).—Numerous analyses, given in full detail, show that the administration of alcohol has no influence on the formation of milk, either qualitatively or quantitatively. With moderate doses, no alcohol passes into the milk; with larger doses, only from 0.2 to 0.6 per cent. of the alcohol given passes into the milk.

W. D. H.

Sodium and Potassium in the Red Corpuscles of the Blood of Animals of different Species, and in Cases of Anæmia caused by Bleeding. By FILIPPO BOTTAZZI and I. CAPELLI (*Real. Accad. Lincei*, 1899, **8**, ii, 65—73).—The authors find that with animals having nuclear red corpuscles, the latter, without exception, contain much more potassium than sodium; of the mammals examined, dog, cat, and rabbit, the last also has red corpuscles richer in potassium than in sodium. It is hence supposed that the red corpuscles of the mammals contain nucleins, the relative quantity of which determines the proportion of potassium present.

The influence of anæmia, especially when serious and protracted, is in all cases to produce a diminution in the amount of sodium and potassium in the red corpuscles. This fact, together with the decrease in the amount of nitrogen under similar circumstances, indicates that whenever the red corpuscles suffer a loss of proteids, a corresponding loss of mineral matter also occurs.

T. H. P.

Sodium and Potassium in the Red Corpuscles of the Blood during Fasting, Phosphorus Poisoning, &c. By FILIPPO BOTTAZZI and I. CAPELLI (*Real. Accad. Lincei*, 1899, **8**, ii, 107—114. Compare preceding abstract).—Fasting and phosphorus poisoning also determine diminutions in the amounts of sodium and potassium in the red corpuscles of the blood, whilst splenotomy gives no such effect. The red corpuscles of the arterial blood of a dog suffering from leucocythemia were found to contain more potassium and less sodium than the normal

From these and former researches (*loc. cit.*), it is concluded that the red corpuscles participate to some extent in the general organic metabolism and in some special cases in the progressive destruction of

the organs and that sodium and potassium are normal constituents of the proteid molecule. T. H. P.

Localisation, Elimination, and Origin of Arsenic in Animals. By ARMAND GAUTIER (*Compt. rend.*, 1900, 130, 284—291. Compare this vol., ii, 152, 168.)—The following organs (human and animal) contain arsenic: thyroid gland, 0.75 mg. per 100 grams; mammary gland, 0.13 per 100 grams; brain, variable quantity, sometimes *nil*; thymus, appreciable amount; hair, horn, skin, milk, and bone, traces only.

No arsenic could be detected in: liver, kidney, spleen, muscle, testicle, seminal fluid, pituitary gland, pancreas, mucous membrane, cellular tissue, salivary glands, suprarenal capsules, ovary, uterus, marrow, blood, urine, and faeces.

In order to ascertain the source of the arsenic found in the above organs, bread, eggs, and fish were examined, but no arsenic could be detected in them.

From these results, it will be seen that those organs which are most commonly examined for arsenic in cases of poisoning are normally free from that substance. Even if the examination be made after putrefaction has set in, and when the small amount of arsenic which is normally present in some of the organs may have possibly diffused throughout the whole system, the dilution of the arsenic would then be so great as to preclude its detection. H. R. LE S.

Universal Distribution of Titanium. By CHARLES BASKERVILLE (*J. Amer. Chem. Soc.*, 1899, 21, 1099—1101).—Beef bone is found to contain 0.0195 per cent., beef flesh 0.013 per cent., human bone, a trace, and human flesh 0.0325 per cent. of titanitic oxide. E. G.

Transformation of Nitrobenzene into Aniline by a Reducing and Hydrogenating Enzyme in the Animal Organism. By J. E. ABELOUS and ERNEST GÉRARD (*Compt. rend.*, 1900, 130, 420—422. Compare Abstr., 1899, ii, 680 and 681).—When the aqueous extract of the kidney of the horse is digested with nitrobenzene and a little chloroform in an atmosphere of hydrogen at 42°, aniline is formed, but no reduction takes place if the extract is previously boiled. It thus appears that the enzyme which has previously been described as having the property of reducing nitrates to nitrites possesses an hydrogenating, as well as a deoxidising, action, a fact which is of importance in connection with the production of animal bases in the organism. N. L.

Excretion of Sulphur in Infants. By WALTHER FREUND (*Zeit. physiol. Chem.*, 1900, 29, 24—46).—The amount of the sulphur in its various forms (sulphates, alkyl hydrogen sulphates, &c.) is given for numerous sucking infants, both in health, and various forms of disease. Many cases are described in detail, and the analyses are arranged in tabular form. General conclusions from the variable results obtained are not easy to draw. W. D. H.

Influence of Peptone and Albumoses on Urinary Secretion. By WILLIAM H. THOMPSON (*J. Physiol.*, 1900, 25, 179—190).—The excretion of proteose or peptone injected into the venous system

of dogs is confined to the hour after the injection. During this time, the output of urinary nitrogen is increased, principally in the form of urea. This, however, is largely due to the salt solution used as the solvent of the proteids. At least 60 per cent. of the injected material is retained in the body; the proportion retained is greatest when deuteroproteose, amphopeptone, or antipectone is used. It is suggested that the proteoses are held in combination as proteose-globulins in the blood.

W. D. H.

Diazo-reactions of Urine. By P. CLEMENS (*Chem. Centr.*, 1899, ii, 1028—1029; from *Deutsch. Arch. klin. Med.*, 63).—An account of numerous experiments made to ascertain the nature of the substance which gives Ehrlich's diazo-reaction in urine, but which led to no very definite result.

E. W. W.

The Pigment of the Arenicolæ. By PIERRE FAUVEL (*Compt. rend.*, 1899, 129, 1273—1275).—There exist in the integument of the *Arenicolæ* two pigments, generally described as distinct, a yellow lipochrome in the epithelial cells, and a black pigment in the form of fine granules in the upper layers of the epidermis. A solution of the lipochrome becomes brown, then black on the addition of various acids; and, it is considered probable that the formation of black granules in the cells is due to a chemical modification of the yellow pigment, under the influence of acidity, produced either in the neighbourhood of the digestive tube, or from the accumulation of waste products, the result of metabolic activity. Details concerning the pigmentation in different species are added.

W. D. H.

Ion-proteid Compounds; the Poisonous Character of Pure Sodium Chloride. By JACQUES LÆB (*Amer. J. Physiol.*, 1900, 3, 327—338).—The experiments recorded were made on fish, medusæ, and cilia. The general conclusions drawn are believed to be also true for air-breathing animals. They principally consist in translating into the new nomenclature which has arisen in connection with the modern theory of solution the work which Ringer did some years ago.

W. D. H.

Physiological Action of Bromine. By F. FESSEL (*Chem. Centr.*, 1899, ii, 885, from *Munch. med. Woch.*, 46, 1270—1273).—The experiments were performed with sodium and potassium bromide. The toxic action of bromine salts is greater in cats than in dogs. The excretion of the bromine does not rise equally with that administered until 'bromine equilibrium' is established with a sufficient dose. The chief amount of the bromide is found in the blood, where it partially replaces sodium chloride. Among the organs, the brain was the only one where it was discovered. Whether bromine will take the place of the iodine of the thyroid, is to be the subject of further work.

W. D. H.

Physiological Action of Protamines and their Decomposition Products. By WILLIAM H. THOMPSON (*Zeit. physiol. Chem.*, 1900, 29, 1—19).—The protamines are toxic; they cause a fall of blood pressure, acting like albumoses on the peripheral vessels directly; blood

coagulation is slowed, and the number of leucocytes in the circulation is lessened. The heart and respiration are also affected. Histons have a very similar action. The substances obtained by the hydrolysis of protamines (protons, hexon bases) have no such effects.

W. D. H.

Physiological Action of Morphine and its Allies. By E. IMPENS (*Pflüger's Archiv*, 1900, 78, 527—596).—The action on respiration was specially investigated. Of the substances used, heroine (diacetylmorphine) produces an effect with the smallest dose; five times as much morphine, twelve times as much dionine (ethylmorphine), twenty times as much codeine are required to produce the same or even a less effect. Peronine (benzylmorphine) has very little action at all. The danger is in about the proportion just quoted, being least with heroine and greatest with codeine. With heroine the energy of breathing and the volume of air inspired are increased, but the act is quieter, and its use is recommended in cases of tuberculosis. The other alkaloids are more uncertain and less sedative in their action. Heroine lessens the amount of oxygen consumed; codeine and dionine increase it at first and then lessen it. Morphine paralyses the irritability of the respiratory centre to stimulation by carbon dioxide, and codeine has a weaker action in the same direction. Dionine, peronine, and heroine do not act in this way. The results obtained from experiments on rabbits are applicable to man.

W. D. H.

Hæmolytic Action of Snake Toxins and Toxic Sera. By J. W. W. STEPHENS (*J. Pathol. and Bacteriol*, 1900, 6, 273—302).—The following general conclusions are drawn from the experiments recorded:—(1) that an antitoxic serum can act on toxins other than, but allied to, that used in the preparation of the serum; (2) that the hæmolytic constituents of snake toxins, and hence snake toxins as a class, are not identical; (3) that against a minimum lethal dose of daboia toxin 0·5 c.c. of Calmette's anti-venom has very little action; (4) that the anti-hæmolytic properties of anti-venomous sera must be increased in order to afford any efficient protective serum, for instance against *Pseudechis* or daboia toxin.

W. D. H.

Sandy Matter from the Human Intestine. By R. S. THOMSON and ALEXANDER R. FERGUSON (*J. Pathol. and Bacteriol*, 1900, 6, 334—338).—Sandy matter, passed with the fæces by a female patient suffering from a dyspeptic condition, was subjected to analysis. It was found to consist of 71·5 per cent. of inorganic, and 28·5 per cent. of organic matter. The inorganic material consisted of calcium carbonate (11·7), tricalcium phosphate (87·3), and insoluble residue (silica) (1 per cent.). Among the organic materials, particular attention was directed to the brown pigment. It was not, however, identified; its solubilities exclude any known derivative of bile pigment. It is possibly an intermediate substance between bile pigment and stercobilin. The sand is readily soluble in dilute acids. It is suggested that it is formed in the ileum, where the intestinal contents are alkaline.

W. D. H.

Milky Serous Effusions. By H. BATTY SHAW (*J. Pathol. and Bacteriol.*, 1900, 6, 339—355).—The appearance of milky, dropsical effusions is familiar to the clinical observer. This is due, in many instances to actual injury to the lacteals and escape of chyle into the body-cavity. In many cases, called chyliform, microscopic examination reveals no fat globules, and chemical examination no great quantity of fat. Often, however, minute particles, probably proteid in nature, are seen; in other cases, the opalescence may be due to proteid in solution. A case of chylous ascites and hydrothorax is here fully recorded, and compared with numerous cases described by others. The cause of the affection was a mass of lymphadenomatous glands pressing on the thoracic duct. There were no visible fat particles in the fluid, and it did not clear with ether, but became jelly-like. The urine also became jelly-like with ether, even when the albumin it contained had been removed by boiling. Normal urine does not behave so, but the same effect was noticed in other cases of albuminuria. The ascitic fluid contained 4 per cent. of solids, 2·2 per cent. of proteid, 0·52 per cent. of fat, and 0·7 per cent. of ash. W. D. H.

Acetonuria. By HUGO LÜTHJE (*Chem. Centr.*, 1899, ii, 972; from *Centr. inn. Med.*, 20, 969—973).—The appearance of acetone in the urine is held to indicate the excessive formation of acids in the organism. As strychnine produces an increased production of acids in the body (Meyer), it was given to animals; but in strychnine convulsions no acetone appears in the urine. In epileptic fits, it is also absent. It is not therefore every acid, including the lactic acids produced by muscular activity, that leads to acetonuria. W. D. H.

Excretion of Diamines in Cystinuria. By P. J. CAMMIDGE and ARCHIBALD E. GARROD (*J. Pathol. and Bacteriol.*, 1900, 6, 327—333).—Another case of cystinuria is added to the four previously recorded in which diamines have been extracted from the urine; it is the second case in which they have been extracted from the fæces also, Baumann and Udranszky's case being the first. A note added to the paper mentions a new case recorded by C. E. Simon (*Amer. J. Med. Sc. Philadelphia*, 1900, 119, 39); here they were found both in fæces and urine. In the present case, cadaverine was present in the urine, putrescine in the fæces. The diamine excretion is extremely intermittent; for no less than twenty-three successive days no diamine was found. This emphasises the necessity for prolonged investigations in other cases.

W. D. H.

Chemistry of Vegetable Physiology and Agriculture.

Reproduction of Yeast without Fermentation in a Limited Supply of Air. By AUGUSTE ROSENSTIEHL (*Compt. rend.*, 1900, 138, 195—198).—The vital activities of yeast cells immersed in sugar solutions manifest themselves in either of two ways, according as to

whether air is freely admitted or not; in the former case, they multiply, and in the latter they induce fermentation. Yeast colonies in apple juice from which air is excluded are frequently seen to grow without evolving any carbon dioxide, although, under these conditions, fermentation should occur. The vitality of the cell seems to be impaired by the tannin or other astringent compounds present, for when these are precipitated by gelatin, fermentation sets in; if excess of gelatin is added, so that these substances are re-dissolved, the yeast cells continue to multiply, but without evolving any gas. The addition of tannin to an artificial wort prevents its fermentation by yeast cells cultivated in apple juice. When the wort is carefully freed from dissolved oxygen, neither fermentation nor reproduction is noticed; the gelatin added to precipitate the tannin has no direct influence on the vitality of the yeast cells. G. T. M.

Decomposition of Diastase during Fermentation. By G. HEINZELMANN (*Bied. Centr.*, 1899, 25, 863; from *Zeit. Spiritusind.*, 1898, No. 41, 357).—In solutions of cane-sugar containing 0.6 per cent. of diastase, it was found that yeast destroys the diastase during fermentation. In the case of malt mash, the diastatic power decreased much less than with sugar solutions; and it was found that the presence of asparagine and other nitrogenous substances economised diastase.

A mixture of starch (160 grams) with water (to 1000 grams), to which diastase (2 grams) was added, lost 14.3 per cent. of diastase in 10 minutes at 61°. During the next 20 minutes (at 62.5°), 45.7 per cent. of the diastase was destroyed, but there was no further change during the next half-hour. N. H. J. M.

Rate of Alcoholic Fermentation. By JAMES O'SULLIVAN (*Bied. Centr.*, 1899, 25, 863; from *Zeit. Spiritusind.*, 1898, 351).—Stirring the liquid expedites fermentation, with or without an excess of yeast. In the case of maltose and dextrose, the rate of fermentation is in proportion to the amount; the rate of alcoholic fermentation of the two substances differs from the rate of the hydrolytic action of yeast on sucrose.

In presence of nutrients, fermentation is quickened, even when the amount of yeast is not increased; the cells have a more healthy appearance than in absence of nutritive matters. N. H. J. M.

Influence of Metals on Broth-cultures of Bacteria. By B. ISACHENKO (*Exper. Stat. Record*, 1899, 11, 123; from *Selsk. Khoz. Lyesov.*, 1898, 189, 35—42).—The results of experiments with *Bacillus spermophilinus* showed that when broth-cultures have to be kept more than a month, only iron vessels may be employed. Tinned iron (or lead), nickel-plated, zinc, or zinc-plated iron vessels are absolutely unsuitable for growing bacteria. Copper apparatus can only be used for keeping the culture of sterilised broth for a very short time. N. H. J. M.

Butyric Acid Fermentation. By ARTHUR SCHATTENFROH and R. GRASSBERGER (*Chem. Centr.*, 1899, ii, 1060—1061; from *Centr. Bakt. Parasit.*, 5, ii, 697—702).—Butyric acid fermentation, at any

rate as regards sugar and starch, seems only to be produced by two very similar bacteria. The one variety of butyric acid bacilli, which is mobile and does not liquefy gelatin, includes the butyric bacillus I. of Gruber, *Bacterium saccharobutyr.* of Kleckli, and others. It occurs in milk, cheese, soil, and in other materials, but is not so common as the second variety which liquefies gelatin and is not mobile.

It seems probable that a pure butyric fermentation of sugar and starch does not exist, and that both the mobile and non-mobile variety always produce lactic acid as well as butyric acid, carbon dioxide, and hydrogen. Just as the quantity of alcohol produced varies, there is a difference in the relative amounts of the two acids. The production of butyric acid depends on the nature of the carbohydrate. Lactose is almost completely fermented to butyric acid by the mobile variety. The non-mobile variety produces from lactose sometimes butyric acid and a small amount of lactic acid, sometimes butyric acid alone. Dextrose, sucrose, and starch are fermented by the mobile variety mainly with production of butyric acid, whilst the non-mobile variety produces more lactic than butyric acid. The latter variety ferments galactose, maltose, and lævulose, but not cellulose and mannitol, and it attacks glycerol only slightly, with production of volatile acids and aldehyde. Both varieties coagulate casein, but without peptonisation. It is proposed to designate both varieties *Granulobacillus saccharobutyr.*, with addition of *immobilis liquefac* and *mobilis non liquefac*.

N. H. J. M.

Bacteria which produce Esters. By ALBERT MAASSEN (*Chem. Centr.*, 1899, ii, 1058—1059; from *Arb. Kais. Ges.-A.*, 15, 500—513).—*Bacillus esterificans*, from putrefying litmus, in broth containing much peptone, produced hydrogen sulphide and mercaptan, but not indole or phenol, and reduced nitrate to nitrite; it did not ferment glycerol or carbohydrates, but decomposed them with production of acid.

Bacillus esterificans fluorescens (from cereals) produces a green, fluorescent dye and, during the first few days, an ester-like aroma, and subsequently an odour resembling that of trimethylamine; it does not peptonise, and reduces nitrates only slightly, does not decompose mannitol or glycerol, but decomposes dextrose and organic acids with production of acid and carbonates. *B. præpollens* (from intestine) peptonises gelatin, decomposes albumin with production of hydrogen sulphide and mercaptan, and produces much ammonium carbonate in cultures containing proteids. In cultivations, in 10 per cent. peptone, two months old, tyrosine, leucine, ammonium propionate, valerate, formate, and succinate, hydrogen sulphide, mercaptan, and an ester (probably amyl) of valeric acid were formed. It rapidly converts urea into ammonium carbonate, but does not produce carbonates from organic salts. It has no effect on nitrates, but decomposes nitrites with liberation of free nitrogen. It is pointed out that the bacillus is the first instance of a microbe which is both beneficial and injurious in agriculture. The bacillus produces esters in all nutritive media (aëration and the presence of proteids are favourable in this respect), and, unlike the

other ester-producing bacilli, retains this property. The aroma produced in milk is very agreeable.

Ester-producing bacilli were isolated from milk, Spree water, soil, and fæces. N. H. J. M.

Magnesia-gypsum as a Solid Medium for the Cultivation of Nitrifying Organisms. By V. OMELIANSKY (*Chem. Centr.*, 1899, ii, 725; from *Centr. Bakt. Parasit.*, 5, ii, 652—655).—The substance, which gave excellent results with nitrous organisms, is prepared by adding a solution of potassium phosphate (0.1), sodium chloride (0.2), magnesium, ammonium, and ferrous sulphates (0.05, 0.2, and 0.04 per cent. respectively) to a mixture of gypsum and magnesium carbonate. The mixture, which should have the consistence of sour cream, is poured on to a glass plate and then transferred to Petri-dishes or test-tubes. Plates sterilised at 120° generally absorb most of the liquid, in which case a sterilised solution of the same composition is added. After inoculation, the substance is kept in a thermostat at 25—30°. N. H. J. M.

Denitrification Bacteria and Sugar. By HJALMAR JENSEN (*Chem. Centr.*, 1899, ii, 1061; from *Centr. Bakt. Parasit.*, 5, ii, 716—720).—In reply to Stutzer and Hartleb (this vol., ii, 97), the author expresses the opinion that the results adduced, as well as his own, do not justify the conclusion that carbohydrates as well as organic salts can serve as source of food and energy for denitrifying bacteria. N. H. J. M.

Decomposition of Nitrates by Bacteria. By S. A. SEWERIN (*Bied. Centr.*, 1899, 25, 854—856; from *Centr. Bakt. Parasit.*, 1897, 504, 554).—Out of 29 bacteria obtained from horse-dung, which were cultivated in broth containing peptone and sodium nitrate (0.3 per cent.), 18 had no effect on the nitrate, 9 reduced the nitrate to nitrite, and 2 (*Bacillus pyocyaneus*, not previously known as a denitrifying organism, and *Vibrio denitrificans*) caused still greater reduction. When the amount of nitrate was less (0.1—0.05 per cent.), 6 of the 9 cultivations reduced the nitrate completely. It is improbable that the whole of the nitric nitrogen was converted into organic nitrogen.

B. pyocyaneus and *V. denitrificans* reduce the whole of the nitrate present in 10 days when the amount is less than 7 grams per litre of broth; potassium nitrate is reduced in greater quantity than the sodium salt. The reduction also proceeds when both cultures are present, but *B. pyocyaneus* hinders the growth of *V. denitrificans*; the latter does not produce nitrites. The exhaustion of broth cultures is due to increasing alkalinity, and addition of phosphoric acid revives the denitrifying power. A portion of the nitrogen is probably converted into organic nitrogen, and a very small quantity into ammonia, when there is a slight surface aëration. Nearly all the nitrogen is liberated in the free state, perhaps mixed with oxides of nitrogen. Both microbes are undesirable in soils, especially as they are destructive both with and without access of air.

Aëration is decidedly a means of hindering denitrification and should be employed as a means of diminishing loss of nitrates.

N. H. J. M

Soil Bacteria. By R. KOLKWITZ (*Chem. Centr.*, 1899, ii, 917; from *Centr. Bakt. Parasit.*, 5, ii, 670—678).—The so-called alinit bacillus is neither *B. megatherium* nor *B. subtilis*. Cultivations of the bacillus made in media prepared from earth-worms (which contain a substance which reduces Fehling's solution, and proteid substances which show the biuret reaction) failed to reduce nitrate, although the bacillus possesses denitrifying properties. N. H. J. M.

Soluble Ferments produced during the Germination of Seeds with Horny Albumen. By ÉMILE BOURQUELOT and HENRI HÉRISSEY (*Compt. rend.*, 1900, 130, 42—44).—The seeds of fenugreek (*Trigonella Fœnum græcum*) and lucerne (*Medicago sativa*) like the carob bean (this vol., ii, 35), when germinating, produce a soluble ferment capable of hydrolysing, in the same manner as hot dilute sulphuric acid, the carbohydrates forming part of certain horny albumens. From the albumens of the carob bean and cassia, these ferments produce mannose and galactose, together with a residue that is not readily attacked by dilute sulphuric acid (compare *loc. cit.*, and *Abstr.*, 1899, i, 839). C. H. B.

Nutrition of Plants with Organic Nitrogenous Compounds. By L. LUTZ (*Exper. Stat. Record*, 1899, 11, 316—317; from *Ann. Sci. Nat. Bot.*, 1899, [viii], 7, 1—103).—Under conditions of sterilisation, phanerogams readily assimilate methylamines, but not benzylamine and pyridine. "Phenolamines" are strong poisons, whilst compound ammonium salts and alkaloids are not available as sources of nitrogen.

Algæ and fungi gave similar results.

The organic nitrogen of beet, fruit, and fish refuse may therefore be made available for plants without nitrification or conversion into ammonia. N. H. J. M.

Regeneration of Proteids from their Products of Decomposition. By DMITRI N. PRIANISCHNIKOFF (*Landw. Versuchs-Stat.*, 1899, 52, 347—381. Compare *Abstr.*, 1899, ii, 787; also Schulze, *ibid.*, 628; Kinoshita, *ibid.*, 1896, ii, 54, and Hansteen, *ibid.*, 1898, ii, 179).—In 1896, Salessky showed that in bulbs of *Allium cepa*, germinating in darkness, there was a possible production of proteids from carbohydrates in conjunction with amino-compounds other than asparagine, the amount of which did not decrease.

In presence of light, proteids are destroyed during germination with as much energy as in darkness. Later, when leaves develop, reproduction of proteids begins: with some plants, 10 to 15 days after germination commences, with other plants (such as *Vicia faba*), much later. Regeneration of proteids takes place either from asparagine and other amides simultaneously, or the utilisation of asparagine lingers behind that of other amino-compounds. No case, however, in which asparagine is chiefly utilised has been observed.

It is probably in the leaves that proteids are regenerated with most energy.

The experiments were made with vetches, peas, beans, yellow lupins, *Cucurbita pepo*, and *Allium cepa*. N. H. J. M.

Decomposition of Chlorophyll by Oxidising Enzymes. By ALBERT F. WOODS (*Chem. Centr.*, 1899, ii, 1126; from *Centr. Bakt. Parasit.*, 5, ii, 745—754).—Oxydases and peroxydases, which regularly occur in small quantity in all higher plants, rapidly decompose chlorophyll. Under certain conditions, not yet understood, the oxydases increase in activity or in quantity, and produce various diseases. The mosaic disease of tobacco is more probably due to enzymes than to Beijerinck's "vivum fluidum."

Oxydases and peroxydases can remain some months in the soil. The former are destroyed within five minutes at 65—70°, the latter in the same time at 80—85°. Oxydases often fail to give the blue reaction with guaiacum extract in presence of egg-albumen. N. H. J. M.

Root Secretions. By FRIEDRICH CZAPEK (*Landw. Versuchs-Stat.*, 1899, 52, 467—475).—A criticism of Kohn's experiments and conclusions (*Abstr.*, 1899, ii, 791). The author, however, considers that electrochemical methods are of importance in physiology (compare *Jahrb. Wiss. Bot.*, 1896, 29, 321, and 1898, 32, 210; also *Ber. deut. bot. Ges.*, 1897, 15, 516). N. H. J. M.

Action of Leguminous Root Nodules in Water Cultures. By FRIEDRICH NOBBE and LORENZ HILTNER (*Landw. Versuchs-Stat.*, 1899, 52, 455—465).—Experiments made with *Robinia pseudacacia* showed, in accordance with what had been previously observed, that root nodules were of little use to the host plant when grown in water culture. The structure of the nodules is altered, and they are filled with water instead of air. On pouring off some of the solution, so as to expose the upper nodules to air, the plant recovered in a few days, and soon produced new leaves of a bright green colour. Similar results were obtained by gradually replacing the water by sand; in this case, the recovery of the plants was slower, and was found to be due to the production of fresh nodules.

Whilst the nodules kept under water seemed to increase very little in size, those above the water increased greatly, many being as much as 45—50 mm. in diameter. In some cases, where the development of the nodules was greatest, the plants themselves became unhealthy, presumably owing to the withdrawal of excessive amounts of nutritive substances by the nodules. In the large nodules, the new year's growth was seen to be distinct from the older portions, and it is thought that in the case of trees a new growth in the nodules is essential for the continued supply of nitrogen.

When nodules which had been kept above the water (in 1897), and were consequently normal, were afterwards (May, 1898) covered with the solution, the growth of the plants was checked, probably owing to the nodules being prevented from forming new growth.

The results make it evident that it is in the nodules, and not in the leaves, that free nitrogen is fixed. N. H. J. M.

Physiological Functions of Solanine. By G. ALBO (*Ann. Agron.*, 1899, 25, 621—622; from A. Borzi, *Contrib. biol. veg.*, 1899, 2, Part 3).—Solanine occurs in all parts, especially in the grain, of several varieties of *Solanaceæ* cultivated under ordinary conditions.

It decreases in amount during germination, and again increases when the plant is well developed. When the plants are screened from light, solanine is found in the shoots during the first period of development, but diminishes in quantity as the reserve substances are used up, and finally disappears altogether; the same occurs in presence of light when the surrounding air is freed from carbon dioxide.

When seeds of *Solanum sodomium* are germinated in the dark until all the solanine has disappeared, and then exposed to light, solanine is again observed as soon as the chlorophyll is well developed. *Solanum melongena*, *S. tuberosum*, and *S. lycopersicum* gave similar results.

It is concluded that solanine is not a migratory form of proteid substances, but a true reserve substance, which the plant utilises during early periods of growth, possibly after hydrolysis by acids or some diastase. Its physiological function is totally different from that of asparagine.

N. H. J. M.

Distribution of Lithium in Plants. By ERICH TSCHERMAK (*Chem. Centr.*, 1899, ii, 1127; from *Zeit. Landw. Versuchs-Wesen. Oesterr.*, 2, 560—572).—A large number of plants from the neighbourhood of Halle a/S and Geneva, and of plants which only occur in Austria, were examined. The results indicate that lithium occurs in plants to a far greater extent than was supposed. In accordance with Focke's observations, lithium is found only in the leaves, the finer portions of the stems, the flowers, and fruit. A list of plants is given in the original paper.

N. H. J. M.

Copper in Plants. By D. T. MACDOUGAL (*Exper. Stat. Record*, 1899, 11, 24; from *Bot. Gaz.*, 1899, 27, 68—69. Compare Abstr., 1896, ii, 486).—The dry wood of a dead specimen of *Quercus macrocarpa* was found to contain nearly 0.05 per cent. of copper which was visible as reddish-brown particles in the tracheides, vessels, and medullary parenchyma. Plants grown in ordinary soils may contain 0.003 per cent. of copper (in the dry matter), whilst according to Lehmann (*loc. cit.*) as much as 0.056 per cent. of copper may be present in plants growing in soils containing much copper.

N. H. J. M.

Presence of Vanadium, Molybdenum, and Chromium in Plants. By EUGÈNE DEMARCAY (*Compt. rend.*, 1900, 130, 91—92).—The ash of Scotch fir, silver fir, vine, oak, poplar, or horn-beam, when treated with boiling water, gives a solution from which hydrogen sulphide precipitates a brown substance, which is soluble in hydrochloric acid. On spectroscopic examination of this hydrochloric acid solution, vanadium, molybdenum, and chromium are found to be present, together with traces of silicon, aluminium, manganese, and zinc.

H. R. LE S.

Green Pigment of Amanita Muscaria. By ARTHUR B. GRIFFITHS (*Compt. rend.*, 1900, 130, 42).—*Amanita (Agaricus) muscaria* contains a green pigment of the composition $C_{29}H_{20}O_{10}$, which dissolves in chloroform and ether, but the solutions show no characteristic absorption bands.

C. H. B.

Poisonous Properties of Sodium Chloride and Sea-water towards Plants. By HENRI COUPIN (*Exper. Stat. Record*, 1899, 11, 24; from *Rev. Gen. Bot.*, 1898, 10, 177—190).—Solutions containing 0.125—5 per cent. of sodium chloride were employed. The toxic strength for the different plants were: vetches, 1.1; peas, 1.2; maize, 1.4; wheat, 1.8, and lupins, 2.2 per cent.

Beta maritima and *Cakile maritima* were killed by a 4 per cent., and *Atriplex hastata maritima* by a 5 per cent. solution. These plants can withstand the amounts of sodium chloride which usually exist in sea-water.

The toxic strength of magnesium chloride and sulphate for these maritime plants is about 2.5 and 3 per cent. respectively.

N. H. J. M.

Effect of Food on the Quality of Milk. By E. O. ARENANDER (*Exper. Stat. Record*, 1899, 11, 184—185; from *Nord. Mejeri. Tidn.*, 1899, 14, 76—77 and 91).—The results of about 2000 analyses of milk showed that the percentage of fat may be reduced 1—2 per cent. below the normal by insufficient food. In Norrland (Sweden), the cows are fed from January to May on a small allowance of poor hay, from June to September on pasture, and from October to December they are liberally fed in stalls. The average amounts of fat found during the three periods are 3.2—3.3, 3.71—4.25, and 3.32—3.52 per cent. Whilst poor feeding will reduce the amount of fat, it is not believed that the fat can be increased above the normal by increasing a normal ration.

N. H. J. M.

Effect of Food on the Quality of Butter. By JOSEF L. HILLS (*Exper. Stat. Record*, 1899, 11, 385; from *Vermont Stat. Rep.*, 1898, 347—350).—The cows received, besides hay and silage, (1) gluten meal, maize meal, and wheat bran; (2) maize and bran; (3) cotton seed, linseed meal, maize, and bran; (4) bran and cotton-seed meal and (5) bran. The butter made from cows fed on ration (4) ranked lowest.

N. H. J. M.

Natural Butter, showing the Sesamé Oil Reaction. By ANTON SCHEIBE (*Bied. Centr.*, 1899, 25, 858; from *Milchzeit.*, 1897, No. 47).—A cow which received, in addition to hay, 2 kilos. of sesamé cake for a week, yielded butter which showed distinctly the Baudouin sesame oil reaction. Pure butter is therefore liable, in Germany, to be considered as adulterated with margarine when sesamé cake is employed as food.

N. H. J. M.

Sesame Oil Reaction of Pure Butter. By PAUL VIETH (*Bied. Centr.*, 1895, 25, 859; from *Milchzeit.*, 1898, 536).—Lehmann (*Protokoll d. Sitz. d. Centralausschusses d. k. Landw. Ges. Hann.*, Jan., 1898) showed that feeding with sesamé cake resulted in milk fat which showed the Baudouin reaction, although very slightly. Reactions of varying strength, which, if not identical with the sesamé oil reaction, differ from it inappreciably, have been universally obtained. It is therefore concluded that the admixture of sesamé oil with margarine is not suitable as a means for enabling the adulteration of butter with margarine to be detected.

N. H. J. M.

Effect of Feeding Cotton and Sesame Cake on Butter. By THOMAS E. THORPE (*Journ. South-Eastern Agr. Coll. Wye*, 1899, No. 8, 64—65).—Three lots of four cows each received, first, linseed cake, and, subsequently, linseed, cotton and sesame cake respectively. At the commencement, the cows received 4 lbs. of cake, in addition to dried grains (4 lbs.), bean meal (2 lbs.), hay and straw (25 lbs.), and roots (40 lbs.); afterwards, the cotton and sesame cake were increased to 6 and 7 lbs., the bean meal being discontinued, and the grains reduced in quantity. Finally, the cows went to grass, and the oil cake was discontinued.

Under the influence of cotton cake, butter was obtained which gave the cotton seed oil reaction; the reacting substance passed into the milk within 24 hours after the cake feeding began, and continued to do so for several days after the cake was discontinued. In the case of mixed milk from several cows, the reaction is, as a rule, less than would be due to 1 per cent. of the oil. In most cases, it would be possible to differentiate between the cotton seed oil reaction due to feeding cotton cake and that due to any considerable addition to butter of margarine containing cotton-seed oil.

In the case of sesame cake, the butter gave no sesame oil reaction, even after the feeding, with as much cake as the cows would eat, had been continued for over two months. With large amounts of cake, the yield of milk was well maintained for some time, but the quality deteriorated and became poor in fat. As the flow of milk decreased, the cows began to get very fat.

N. H. J. M.

Nutritive Value of Asparagine. By B. K. BRUTSKUS (*Exper. Stat. Record*, 1899, 11, 275—276; from *Zap. Novo-Alexandri Inst. Selsk. Khoz. Lyesov.*, 1898, 11, 145—228. Compare Bahlmann, *Abstr.*, 1887, 512).—Experiments are described in which rabbits were fed with rice starch (640), birch sawdust (120), sugar (75), oil (30), salt (20), hay ash (20), barley ash (10), and water (34.4 grams), both with addition of and without, asparagine (150 grams). When no asparagine was given, the amount of starch was 725 grams. The nitrogen of the fæces and urine were determined.

The results indicate that the value of asparagine is much greater than that of an isodynamic amount of starch, and, that whilst asparagine cannot take the place of protein in a diet, it may economise about one-fourth of the protein in the body which would be consumed if the food contained no nitrogen.

N. H. J. M.

Vegetation Experiments in 1897. By DMITRI N. PRIANISCHNIKOFF (*Bied. Centr.*, 1899, 25, 809—815. Compare *Abstr.*, 1899, ii, 514).—Sand culture experiments were made in which barley was manured with the same amount of nitrogen in different forms. The relative yields with the different manures were: sodium nitrate, 100; blood meal, 56; stable manure, 15; and fæces, 6.5. Further experiments are described in which the various manures (N=0.5 gram) were applied to a poor, sandy soil manured with potassium sulphate. Taking the yield of the pots which had no nitrogen as 100, the yields were as follows: urine, 182; green manure (clover leaves), 156; stable

manure, 150 ; ammonium sulphate, 132 ; sodium nitrate, 126 ; blood meal, 113 ; and faeces, 86.

As regards the effect of different amounts of water in the soil on the growth of plants, it is concluded that dryness of the soil does not cause greater rapidity of growth, and that early crops in dry seasons are due to increased temperature and greater amount of light.

N. H. J. M.

Influence of Fermentation on the Value of Hay. By FRIEDRICH HOLDEFLEISS (*Mitt. Landw. Inst. kgl. Univ. Breslau*, 1899, *Heft.* 1, 59—74).—Haymaking is essentially a process of fermentation in which the amount of crude fibre is diminished whilst the remaining crude fibre is probably loosened. The amounts of other food constituents, especially the nitrogen-free extract, are relatively increased, and the hay not only acquires a better taste but its digestibility is probably greater when properly made than when dried too quickly.

Fermentation seems to diminish the amount of pentosans in hay, or at any rate in grass hay. In the one experiment with clover hay, the amount of pentosans differed very slightly in the dry matter of hay which took 9 and 16 days respectively to make (17·69 and 17·26 per cent.).

N. H. J. M.

Cultivation of White Lupins. By PIERRE P. DEHÉRAIN and E. DEMOUSSY (*Compt. rend.*, 1900, 130, 20—24).—The results of experiments extending over three years showed that white lupins only develop satisfactorily when their roots are provided with nodules, and that the nodules vary in form and size according to the source of inoculation. Nodules were produced by inoculation from vetches and from lucerne as well as from soil.

In suitable soil, the nodules are small and contain forked bacteroids, which were not found in the large nodules ; vigorous plants are then produced the dry matter of which may contain as much as 3 per cent. of nitrogen. Plants with large, smooth nodules surrounding the root contained 2 per cent. of nitrogen in the dry matter. In some cases, very large nodules like raspberries were produced ; these seem to act as parasites, the plants being much less nitrogenous ($N = 0\cdot6 - 0\cdot8$ per cent. in the dry matter).

Hairy vetch inoculation produced hemispherical nodules, whilst lucerne inoculation produced detached nodules ; the dry matter of the host plants contained 1 per cent. of nitrogen.

The frequent failure of white lupins at Grignon is attributed to absence of suitable microbes in the soil rather than to the presence of lime.

N. H. J. M.

Experiments on Potatoes. By JAMES S. GORDON (*Cheshire County Council Rep.*, 1899).—Farmyard manure gave much better results than artificial manures alone, but addition of artificial manures to farmyard manure was beneficial. Ammonium sulphate gave better results, both as regards yield and quality, than sodium nitrate, and potassium chloride produced a greater yield and better potatoes than kainite.

N. H. J. M.

Tobacco Plant. By JOHANNES BEHRENS (*Land. Versuchs-Stat.*, 1899, 52, 431—454. Compare Abstr., 1899, ii, 745).—The substance to which the brown colour of tobacco is due is not present in the fresh leaves, but is produced shortly before the natural death of the leaves when the carbohydrates are mostly consumed. When the chromogen is once formed, its oxidation proceeds in the dead leaf when sufficient moisture is present; light is unnecessary. The supposition that only ripe leaves can become brown is shown to be incorrect. Green leaves which have been killed by chloroform are unable to acquire a brown colour.

Tobacco leaves contain glucosides (probably several) and emulsin. It is thought probable that the chromogen is produced from a glucoside (compare O. Loew, *Rep. No. 59, U.S. Dept. of Agric.*, 1899).

N. H. J. M.

Experiments with Tobacco Fertilisers, 1892—1896. By EDWARD H. JENKINS (*Ann. Rep. Agr. Expt. Stat. Connecticut*, 21, for 1897, 243—256).—Whilst no manure will always produce the best results even on the same land, owing to the effects of climate, certain manures gave on the whole better results than others.

The liberal, but not greatly excessive, amounts of available plant food required for a good crop of tobacco may be applied in a variety of forms, and occasional changes in the forms of nitrogen and potash may be advantageous. Large amounts of chlorides and sulphates injure the quality of the leaves.

N. H. J. M.

Effect of Fertilisers on the Composition of Wrapper Leaf Tobacco. By EDWARD H. JENKINS (*Ann. Rep. Agr. Expt. Stat. Connecticut*, 20, for 1896, 322—333).—Field experiments are described in which the same manures (mostly vegetable matters, with and without addition of minerals) were applied to the same plots for four or five years.

The short wrappers were found to contain rather more ash, ether extract, and nitrogen-free extract than the long ones, and correspondingly less fibre, nicotine, nitrates, and proteids.

The different manures had no effect on the amounts of ether extract, fibre, and nitrogen-free extract; but an excess of nitrogenous manure resulted in a much larger percentage of nitrates in the leaf, amounting in one case to 1.56 per cent. of nitric nitrogen, and the percentages of proteids and nicotine were also raised. Potash manures increased the amount of potassium in the leaf ash, but the effect varies greatly with the same quantity of potassium in different forms. The leaves of plants manured with potassium sulphate may contain even less potassium than those of plants which receive half the amount of potassium in the form of carbonate. The leaf ash containing the highest amount of calcium (and the least amount of potassium) was obtained by manuring with potassium sulphate.

Tobacco manured with stable-manure yielded an ash containing five times as much chlorine as the ash from any of the other plots.

N. H. J. M.

Manurial Experiments on Permanent Pasture. By W. J. MALDEN (*East Sussex County Council Rep.*, 1899).—The soil on which the experiments were made was more or less exhausted by dairying and stock raising, and the pasture poor. As regards mineral manures, phosphoric acid, in which the soil was deficient, gave much the best results when applied in the form of basic slag. Kainite had very little effect.

Nitrogen as sodium nitrate was useless without phosphates, whilst ammonium sulphate alone slightly improved the quality of the grasses. In conjunction with basic slag, sodium nitrate produced inferior grasses as compared with basic slag and ammonium sulphate.

Farmyard manure, in conjunction with basic slag, gave a great increase in weight, and at the same time improved the quality.

Detailed results of botanical separations of the herbage of the various plots are given as well as percentages of gramineous, leguminous and miscellaneous plants. N. H. J. M.

Field Experiments for determining the general Manurial Requirements of Typical Soils with Reference to Chemical Soil Analysis. By P. BAESSLER (*Bied. Centr.*, 1899, 25, 815—820; from *Ber. Agrik.-Chem. Versuchs-Stat. Köslin* for 1897, 45).—Field experiments were made on soils of different kinds after the soil had been analysed by the official methods. The total and citrate soluble phosphoric acid, the total calcium and calcium carbonate, potassium soluble in 10 per cent. hydrochloric acid, and the nitrogen were determined.

The results of field experiments showed that relations existed between the effects of potash manures and the percentage of potassium in the soil; in the case of phosphoric acid, the results were more irregular, whilst with nitrogen the results were indefinite.

With lime and complete minerals, 21 per cent. of the phosphoric acid was utilised; in absence of potassium and in absence of nitrogen, only 18 and 14 per cent. respectively of the phosphoric acid was utilised. When nitrogenous manure alone was applied, only 28 per cent. of the nitrogen of the manure was taken up by the crop, the amount being increased to 59, 74, and 86 per cent. respectively, when in addition to nitrogen, potassium, phosphoric acid, and complete minerals respectively were applied.

Analyses of the soils and of the crops are given. N. H. J. M.

Pot Experiments on the Action of Lime and Magnesia in Burnt Lime and Marls. By RICHARD ULBRICHT (*Landw. Versuchs-Stat.*, 1899, 52, 383—430).—A large number of experiments are described in which different amounts of calcium and magnesium oxides and carbonates were applied to different plants, chiefly lupins.

Even with abundance of potash, lupins were injured by slight amounts of lime, and 500 or 1,000 kilos. of lime per morgen caused a considerable reduction in the yield. Lime, containing magnesia (250 kilos.) gave irregular results, but 500 kilos. of the mixtures much reduced the yield, especially when the percentage of magnesia was high. Similar results were obtained with barley and vetches. In experiments with lupins after radish, it was found that the injurious effects of excessive liming extended to the second year.

Application of powdered magnesite (MgCO_3 , 76.4; CaCO_3 , 18.4 per cent., 500 kilos. per morgen) applied in the spring increased the yield of lupins considerably.

Calcium carbonate, as marls and powdered marble, invariably reduced the total yield of the leguminous plants when applied in large amounts, but in the case of lupins to a less extent than burnt lime. (compare R. Heinrich : *Mergel und. Mergeln Berlin*, 1896).

N. H. J. M.

Analytical Chemistry.

Ammonium Dithiocarbonate as a Substitute for Hydrogen and Ammonium Sulphides. By M. VOGTHERR (*Zeit. anal. Chem.*, 1900, 39, 44; from *Ber. deutsch. pharm. Ges.*, 8, 228).—The reagent is prepared by shaking 5 parts of carbon disulphide with 9 parts of 22 per cent. ammonia until it is completely dissolved. Hydrochloric or acetic acid is then added until the precipitate produced dissolves only slowly, and the mixture is diluted with water to three or four times its volume. In most, but not in all cases, this reagent can be employed instead of hydrogen sulphide or ammonium sulphide, and in the original paper a scheme for its employment in qualitative analyses is drawn up. M. J. S.

Volumetric Estimation of Hydrogen. Diffusion of a Solid into a Gas. By ALBERT COLSON (*Compt. rend.*, 1900, 130, 330—332. Compare this vol., ii, 140).—Silver hydroxide, obtained by adding a solution of potassium hydroxide to a solution of silver nitrate, when dried at 110—120°, has very nearly the composition AgOH. This compound absorbs hydrogen even at 0°, but more readily when heated at 100°, water and metallic silver being produced; neither methane, ethane, nor oxygen are absorbed by it, so that it may be used for the estimation of hydrogen in a mixture of one or more of the above gases.

At 0°, the rate of absorption of hydrogen by silver hydroxide does not vary with the amount of surface of solid in contact with the gas. When the amount of hydroxide present is from 2.0—0.75 grams, then the rate of absorption is practically constant, and this may be explained, if we assume that, in the presence of hydrogen, the hydroxide exerts a true vapour pressure. The reduced silver is deposited along the sides of the tube and not at the place where the hydroxide originally was, and since this phenomenon occurs even at 0°, it must be regarded as a true example of the diffusion of a solid into a gas.

H. R. LE S.

Iodometric Process for the Analysis of Mixtures of Chlorate and Hypochlorite. By HUGO DITZ and HEINRICH KNÖPFELMACHER (*Zeit. angew. Chem.*, 1899, 1195, 1198, 1217—1220).—Chlorates, in the presence of potassium iodide and hydrochloric acid, liberate iodine,

but the reaction is slow and uncertain and therefore not suitable for quantitative purposes. If, however, a solution of a chlorate is mixed with potassium bromide and a sufficiency of hydrochloric acid, bromine is liberated quantitatively and may then be estimated by the usual iodometric method. Hypochlorites behave similarly. 25 c.c. of the solution containing approximately 0.06 gram of the chlorate are mixed in a generating flask with 20 c.c. of a 5 per cent. solution of potassium bromide and 50 c.c. of strong hydrochloric acid are added from a separating funnel, the air which escapes from the flask passing through a bulb containing solution of potassium iodide to retain any bromine vapour. After 1 hour, the liquid is titrated as usual. Any hypochlorite is estimated by the Penot method and allowed for.

L. DE K.

Estimation of Sulphuric Acid in the presence of Iron. III. By FRIEDRICH W. KÜSTER and A. THIEL (*Zeit. anorg. Chem.*, 1900, 22, 424—444. Compare Abstr., 1899, ii, 247 and 611).—A large number of experiments on the estimation of sulphuric acid in the presence of iron gave the following results. When a hot solution of sulphuric acid containing ferric salts is precipitated with barium chloride, the barium salt of the complex ferrisulphuric acid, $\text{Ba}(\text{Fe}_2\text{S}_2\text{O}_8)_2$, is contained in the precipitate, and this causes a loss which may amount to as much as 7 per cent. of the sulphuric acid. This formation of the complex salt can be prevented (i) by previous precipitation of the ferric salt with ammonia (ii) by converting the ferric salt into a complex salt, as, for instance, with ammonium oxalate; (iii) by precipitation in the cold, and (iv) by adding the hot solution of sulphuric acid and ferric salt to the barium chloride. The conversion of the ferric salt into ferrous salt by means of zinc, &c., is not recommended, for although the loss due to the formation of the complex acid is avoided, other much smaller errors are introduced by the precipitation of zinc sulphate and ferrous sulphate together with the barium sulphate.

E. C. R.

Estimation of Nitric Acid in Water. By MAX HÖNIG (*Chem. Centr.*, 1199, ii, 1032; from *Festschr. Hochschule Brünn*, 1899).—The Marx-Trommsdorff process is recommended. The sample should contain about 0.001 gram of nitric pentoxide per 25 c.c. and must therefore, if needful, be suitably diluted or concentrated.

The indigo solution is prepared by dissolving 1.4200 grams of sodium or 1.5407 grams of potassium indigotintrisulphonate in 1 litre of water; of this, 5.5 c.c. mixed with 50 c.c. of sulphuric acid are used in the test.

L. DE K.

Estimation of Nitrates. By CHARLES M. VAN DEVENTER (*Zeit. physikal. Chem.*, 1899, 31, 50—58).—A new method is described, depending on the brown coloration produced on mixing solutions of ferrous sulphate and a nitrate in presence of sulphuric acid. If the ferrous sulphate solution is gradually added to the nitric acid solution, the brown coloration, which is due to the evolved nitric oxide dissolving in the ferrous sulphate solution, is not persistent until all the nitric acid has been used up in oxidising the ferrous salt. As the accuracy of the

reaction necessitates the absence of air, the method is carried out as follows. A non-graduated tube, open at one end and fitted at the other with a tap and funnel, is filled with mercury and placed funnel upwards in a mercury trough; into this tube about 1 c.c. of bromoform is introduced in order that the nitric and sulphuric acids may not come into direct contact with the mercury. By means of the funnel and tap, a measured volume (5 c.c.) of the nitrate solution, and, after the funnel has been washed with a little water, 8 c.c. of concentrated sulphuric acid are brought into the tube. Standardised ferrous sulphate solution is then allowed to flow up into the tube from a burette with a turned up point; when the end of the reaction is near, a further 8 c.c. of concentrated sulphuric acid are added by the funnel and the addition of the ferrous solution carefully continued until the liquid in the tube is of a distinct reddish-brown tint, the volume of ferrous solution added being read off. The presence of an excess of ferrous salt is confirmed by pouring the contents of the tube into water and adding potassium ferricyanide solution. Although it is known that 1 mol. of nitric acid oxidises 3 mols. of ferrous salt, it is best to determine the strength of the ferrous solution by carrying out a test with a nitrate solution of known strength. The funnel tube should not be too long, or the contents are liable to become too cold.

As regards substances interfering with the process, coloured solutions are of course inadmissible, as also is the presence of compounds giving a precipitate or coloration with sulphuric acid. Any carbonates in the liquid to be tested should be removed by the addition of a little acid.

T. H. P.

Detection and Estimation of very small quantities of Nitrous Acid. By HUGO ERDMANN (*Ber.*, 1900, 33, 210—215).—1-Amino-8-hydroxynaphthalene-4:6-disulphonic acid, which is prepared from 1:3:5-naphthalenetrisulphonic acid by nitration, reduction and treatment with soda (*Chem. Ind.*, 1898, 523), gives in acid solution a bright Bordeaux-red coloration with nitrous acid. The reaction is more delicate than that given by the other reagents proposed for the detection of nitrous acid in water, and is employed in the following manner: 50 c.c. of the water to be tested are mixed with 5 c.c. of an acidified solution of sodium sulphanilate (containing 2 grams of the sodium salt per litre) and about 0.5 gram of the solid aminonaphtholdisulphonic acid added in the form of acid sodium salt mixed with sodium sulphate. The coloration reaches its maximum intensity in about an hour and may be compared colorimetrically with that produced by a known amount of a standard nitrite solution.

A. H.

Estimation of Phosphoric Acid Soluble in a 2 per cent. Solution of Citric Acid. By ALEXANDER HERZFELD (*Chem. Centr.*, 1899, ii, 1139; from *Zeit. Ver. Rüben-Zuck. Ind.*, 1899, 862—863).—When basic slags are treated with a 2 per cent. solution of citric acid, a notable amount of silicic acid dissolves, and passes first into the phosphomolybdate and afterwards into the magnesium phosphate precipitate. In one instance, the amount of phosphoric acid as estimated in this manner was found to be 3.6 per cent. in excess of the truth.

L. DE K.

Phosphates and the Humic Acid Process. By WILHELM HOFFMEISTER (*Landw. Versuchs-Stat.*, 1899, 52, 329—345. Compare Abstr., 1898, ii, 538).—In the extraction of phosphates by ammonium humate, the lime of the calcium phosphate is converted into carbonate or humate, whilst the phosphoric acid enters into combination with ammonia and alkalis. The solution takes place most readily in such phosphates as superphosphate and basic slag.

Silicic acid always dissolves along with the phosphoric acid, and as a rule the silica dissolved increases with the phosphoric acid. The presence of soluble silica increases the solubility of the phosphoric acid, so that more phosphoric acid is dissolved when fresh sand (containing soluble silica) is employed than with exhausted sand. It was found that whilst 150 grams of pure sand yielded 0.0104 gram of silica soluble in ammonium humate, the addition of 5 grams of sodium phosphate increased the amount of silica to 0.0368 gram.

It is probable, therefore, that in soils the soluble silica is of importance in increasing the availability of the phosphoric acid, and it is supposed that the supply of soluble silica becomes periodically exhausted.

Estimations of phosphoric acid and potash in soil were made by the humic acid method, and the results compared with the amounts dissolved by hydrochloric acid.

N. H. J. M.

Biological Detection of Arsenic in Skin, Hairs, Perspiration, and Urine. By W. SCHOLTZ (*Chem. Centr.*, 1899, ii, 1032—1033; from *Berl. klin. Woch.*, 36, 913—915).—Abba's process of acting on these substances with the fungus *Penicillium brevicaulis* and observing the garlic odour given off after some time if arsenic should be present, is much more delicate than Marsh's test: even 1/200—1/500 part of a milligram may still be detected.

The odour of urine, which interferes somewhat with the test, may be removed by means of animal charcoal.

L. DE K.

Stannous Chloride and Bettendorf's Test for Arsenic. By F. DIETZE (*Zeit. anal. Chem.*, 1900, 39, 44—45; from *Pharm. Zeit.*, 1897, 191).—Stannous chloride, to be fit for use in Bettendorf's test, must be free from ammonium salts, sulphates, iron and arsenic, all of which, besides other impurities, may be present in the commercial salt. When a solution of 1 gram dissolved in 5 c.c. of hydrochloric acid of sp. gr. 1.19, is boiled for several minutes, the solution must remain clear and colourless for an hour. When titrated with iodine, it should show a purity of at least 98.5 per cent.

M. J. S.

Bettendorf's Arsenic Test. By HENRIK ENELL (*Zeit. anal. Chem.*, 1900, 39, 45; from *Nord. Farm. Tidsskrift.*, 1896, No. 12).—Arsenic acid is much more slowly reduced by stannous chloride than is arsenious acid; heat accelerates the reaction. To detect traces of arsenic, the author filters the liquid through a very small filter, which is then spread out upon white paper. Arsenic appears as a reddish-brown stain.

M. J. S.

Bettendorf's Arsenic Test. By G. FRERICHS (*Zeit. anal. Chem.*, 900, 39, 45—46; from *Apoth. Zeit.*, 1897, 176).—The reaction is

capable of detecting 0.06 milligram of arsenic in the form of arsenic acid or 0.013 milligram in the form of arsenious acid. Gutzeit's test is equally sensitive. The test cannot be absolutely depended upon; traces of mercury may be mistaken for arsenic. M. J. S.

Constitution of the Ammonium Magnesium Arsenate of Analysis. By MARTHA AUSTIN (*Amer. J. Sci.*, 1900, [iv], 9, 55—61).—A precipitate of ideal condition may be obtained by adding to the faintly acid solution of an arsenate (not exceeding 200 c.c.) magnesia mixture (110 grams of crystallised magnesium chloride, and 58 grams of ammonium chloride are dissolved in water and diluted to 2 litres; 10 c.c. of ammonia are then added) amounting to about 30 c.c. in excess of that theoretically needed. The precipitate is collected and transferred to the filter by means of the filtrate, when washing with about 25 c.c. of faintly ammoniacal water will be sufficient to free it from soluble impurities. No arsenic will be found in the filtrate or washings. If, however, the liquid contains excess of ammonium chloride, a precipitate is obtained which is richer in ammonia and yields on ignition a residue containing some meta-arsenate. Much ammonium chloride also increases the solubility of the compound, although this is again lessened by excess of magnesia mixture. L. DE K.

Estimation of Carbon, Copper, and Manganese in Iron By OTTO HERTING (*Zeit. angew. Chem.*, 1899, 1193—1194).—A reply to Murmann on the subject of the estimation of carbon, copper, and manganese in pig-iron, wrought-iron, and steel.

Heid's process is recommended for the estimation of the carbon. The iron is dissolved in copper-ammonium chloride, the impure carbon is collected on an asbestos filter, and well washed with hot water, and then with alcohol and ether. The filter is transferred to a Rose's crucible, dried at 120°, and weighed; the carbon is then burnt in a current of oxygen, and is represented by the loss in weight. To estimate graphite, the sample is dissolved in dilute nitric acid and the insoluble matter treated as above. Murmann's statement, that the copper cannot be estimated in the liquid obtained when dissolving the sample in hydrochloric acid for the purpose of estimating the sulphur, is baseless, as small quantities of copper entirely dissolve.

Manganese is best estimated volumetrically.

L. DE K.

Microchemical Detection of Potassium, Rubidium, Cæsium, Indium, and Thiosulphates. By A. C. HUYSE (*Zeit. anal. Chem.*, 1900, 39, 9—11).—Sodium bismuth thiosulphate, prepared as follows, is a highly sensitive reagent for the detection of potassium, cæsium, and rubidium. A little basic bismuth nitrate is dissolved in the smallest possible quantity of hydrochloric acid, and water is added until a thick, white precipitate is formed, which is then dissolved by the addition of sodium thiosulphate, avoiding excess. Strong alcohol is added until a permanent turbidity is produced, and this is cleared up by adding a little water. The reagent must be freshly prepared. The liquid to be tested must either be evaporated to dryness on a glass slide, or mixed with the same

proportion of alcohol as is contained in the reagent. Salts of potassium, caesium, and rubidium give with this reagent characteristic, yellowish-green, acicular, monoclinic crystals. Salts of the alkaline earths produce a white precipitate, which cannot be confused with the above, but salts of ammonium and the other metals give no precipitate, and do not interfere with the test. Visible crystals were obtained from 0.002 mg. of potassium nitrate.

Caesium chloride produces, in solutions of indium sulphate containing a little free sulphuric acid, octahedra of caesium indium alum. Ammonium fluoride also produces octahedral crystals, resembling those obtained from aluminium salts. For the employment of these two tests, aluminium, and, for the latter, iron, must be absent. Mercuric thiocyanate is also a sensitive reagent, yielding crystals which differ somewhat from the zinc and cadmium mercuric thiocyanates. Oxalic acid and ammonium oxalate are highly sensitive tests, producing crystals which resemble zinc oxalate, but are insoluble in ammonia. These two reactions are only characteristic of indium in the absence of zinc, cadmium, cobalt, copper, and iron.

Minute quantities of sodium thiosulphate (0.01 mg.) can be detected by adding thallous nitrate in excess, when tabular and cruciform crystals are formed. Sulphates, nitrates, and acetates do not interfere with the reaction, but haloid salts prevent it.

M. J. S.

Precipitation of Silver Chloride by Dimercurous Ammonium Chloride. By F. LETEUR (*Compt. rend.*, 1900, 130, 248—250).—In the ordinary method for the detection of silver in the presence of mercurous salts, the chlorides of the two metals are treated with ammonia, and if the silver chloride is present in relatively large quantities, a considerable amount is rendered soluble. When the mercurous salt preponderates, a large proportion, or even the whole, of the silver chloride remains undissolved, the precipitate of dimercurous ammonium chloride always retaining a notable quantity of the silver salt; under these conditions, the insoluble portion is treated with aqua regia, in order to convert the mercury compound into soluble mercuric chloride, and the final residue is examined for silver.

G. T. M.

Estimation of Calcium by the Citrate Method. By MAX PASSON (*Zeit. angew. Chem.*, 1899, 1153—1155. Compare Abstr., 1898, ii, 642).—The process has been slightly modified. Instead of a 10 per cent., a 2 per cent. solution of citric acid is employed. The solution containing the calcium, and also iron, aluminium, and perhaps phosphoric acid, is neutralised with ammonia, and the precipitate formed redissolved by means of the citric acid solution; 20 c.c. more of this are then added, and after diluting with water, the solution is heated to boiling and precipitated with large excess of ammonium oxalate.

Manganese, if present to any large extent, must be previously removed. It has been found that the results are trustworthy; those obtained by precipitating the iron and aluminium by the acetate method, and then precipitating the calcium in the filtrate, are in excess of the truth.

L. DE K.

Estimation of Thallium as the Acid and Normal Sulphates. By PHILIP E. BROWNING (*Amer. J. Sci.*, 1900, 9, 137—138).—Thallium may be accurately weighed as normal sulphate, as already suggested by Crookes. The solution containing thallous nitrate or chloride is mixed with sulphuric acid, evaporated to dryness, and gradually heated to redness, until the weight is constant. Normal thallous sulphate is thus formed.

The author states that, by drying at 220—240° to constant weight, the acid sulphate is obtained, which may then be weighed. The results are quite satisfactory. L. DE K.

Detection of Copper. By DIOSCORIDE VITALI (*Chem. Centr.*, 1899, ii, 990—991; from *Boll. Chim. Farm.*, 38, 665—668).—See this vol., ii, 208.

Estimation of Mercury in Urine. By SCHUMACHER and W. L. JUNG (*Zeit. anal. Chem.*, 39, 12—18).—A litre of the urine is warmed on the steam-bath, with addition of 100 c.c. of concentrated hydrochloric acid and 15—20 grams of potassium chlorate, in a flask with inverted condenser. When the mixture, which at first is deep red, has become pale coloured, it is left for 12 hours in the cold to complete as far as possible the destruction of the organic matter by the nascent chlorine. It is then warmed to expel most of the chlorine, and precipitated with about 100 c.c. of strong, clear, stannous chloride solution. The precipitate is collected on an asbestos filter, which is then transferred to a small flask and warmed with potassium hydroxide solution. Potassium chlorate and excess of hydrochloric acid are again added, by which means the last traces of organic matter are destroyed and the mercury again dissolved. The solution is filtered, and again reduced with stannous chloride. The mercury is now collected on a filter of gilt asbestos mixed with small granules of gold. The gilt asbestos is prepared by steeping purified asbestos in a strong solution of gold chloride, and reducing by heating for 15 minutes in pure hydrogen; it is then washed with dilute hydrochloric acid and hot water, and dried. Such a filter arrests every trace of mercury. The filter is then washed with hydrochloric acid, water, alcohol, and ether, and dried in a current of dry air until its weight is constant. It is then heated strongly enough to expel the mercury from the gold amalgam and again weighed. Test analyses in which 2·5 and 4·4 mg. of mercury (in the form of mercuric chloride) were added respectively to a litre of urine, gave fairly close results, but when less than 1 mg. is present the results are only approximate. M. J. S.

New Method of Estimating Aluminium. By ALFRED STOCK (*Compt. rend.*, 1900, 130, 175—178, and *Ber.*, 1900, 33, 548—553).—When a neutral or slightly acid solution of aluminium sulphate is treated with excess of a solution containing potassium iodide (5 mols.) and potassium iodate (1 mol.), iodine is liberated, and aluminium hydroxide is precipitated in accordance with the following equation: $\text{Al}_2(\text{SO}_4)_3 + 5\text{KI} + \text{KIO}_3 + 3\text{H}_2\text{O} = 2\text{Al}(\text{OH})_3 + 3\text{K}_2\text{SO}_4 + 3\text{I}_2$. The free iodine is removed by adding sodium thiosulphate, and the mixture heated to boiling, the hydroxide being thus obtained as a flocculent precipitate readily filtered and washed. The precipitation is complete, and unless

a large excess of sulphate is present in the original solution, the product is free from sulphur. When phosphoric acid is present, the precipitate, after ignition, has the composition $2\text{Al}_2\text{O}_3 \cdot \text{P}_2\text{O}_5$. If the mixture is heated for one hour, and if sufficient potassium iodide is added to redissolve the liberated iodine, the use of thiosulphate may be avoided and the aluminium hydroxide thus produced is even more amenable to subsequent treatment, but on account of the difficulty attending the filtration of a hot solution of iodine the author recommends the first method.

G. T. M.

Estimation of Titanic Acid in Iron Ore. By JAS. BRAKES (*J. Soc. Chem. Ind.* 1899, 18, 1097).—One gram of the ore is dissolved in hydrochloric acid, the solution is diluted and filtered; the undissolved matter is fused with potassium-sodium carbonate, the fused mass dissolved in hydrochloric acid and united with the main solution. After nearly neutralising with ammonia, 50 c.c. of sulphurous acid are added, and when the liquid has become colourless it is boiled for 30 minutes, the volume being kept constant with sulphurous acid. This causes a precipitate of titanous oxide, which is then collected and washed with hot water. After burning it in a platinum crucible, it is moistened with dilute sulphuric acid, a few c.c. of hydrofluoric acid are added, the whole is evaporated to dryness to expel any silica, and then strongly ignited; the titanium is then weighed as dioxide.

L. DE K.

Quantitative Separation of Tin, Antimony and Arsenic. By RICHARD MARBURG (*Zeit. anal. Chem.*, 1900, 39, 47—56).—The author reproduces Dancer's paper on this subject (*Abstr.*, 1898, ii, 311) with remarks on the various stages of the process. He confirms the exactness and convenience of the lime method for separating tin from antimony, but regards the separation of arsenic and antimony in the filtrate as less exact, and prefers to operate as follows. The antimony and arsenic are precipitated as sulphides, which after washing are digested with a large quantity of potassium hydroxide. The solution is saturated with chlorine and the two metals then separated by Bunsen's method (*Annalen*, 1878, 192, 317). In this separation the presence of too much hydrochloric acid must be avoided. The antimony pentasulphide must be converted into trisulphide by prolonged heating at 230° in Paul's apparatus (*Abstr.*, 1893, ii, 90), but it is better to convert it into tetroxide. Sulphides of the three metals, when precipitated by hydrogen sulphide from an acid solution, are very slowly attacked by lime-water; it is preferable to redissolve them in colourless potassium sulphide and reprecipitate by an acid in the cold.

M. J. S.

Simplification of the Phenylhydrazine Test for Sugar. By ALBERT NEUMAN (*Chem. Centr.*, 1899, ii, 1033; from *Arch. Anat. Phys. Physiol. Abt.*, 1899, *Suppl.*, 549—552).—5 c.c. of the liquid to be tested, for example, diabetic urine, are mixed with 2 c.c. of acetic acid previously saturated with sodium acetate, 2 drops of phenylhydrazine added, and the liquid concentrated to 3 c.c. When cold, characteristic crystals of the osazone will be noticed if sugar is present.

L. DE K.

Estimation of Sucrose in Condensed Milk. By LEO GRÜNHUT and SEVERIN H. R. RIIBER (*Zeit. anal. Chem.*, 1900, **39**, 19—36).—For the estimation of two sugars occurring together, three methods are possible; (1) Estimation of the reducing power before and after inversion; (2) estimation of the optical rotation before and after inversion; (3) estimation of reducing power and rotation without inversion. The authors discuss the advantages of the three methods for the purpose of estimating the sucrose in condensed milk in the presence of the lactose, and find the first and third methods wholly inapplicable. The second method, with certain precautions, gives satisfactory results. The solution must be prepared by treating the condensed milk with boiling water and cooling the solution to exclude the influence of multirotation. Hydrochloric acid is employed for the inversion. If used according to the so-called *Zollvorschrift* (*Zeit. anal. Chem.*, **32**), it is found to have no influence on the rotatory power of any of the constituents of normal milk. Both the optical observations must be made at exactly the same temperature; 20° is preferred. Lead acetate, avoiding a large excess, may be employed for precipitating the casein, &c., but the volume of the precipitate must not be neglected. The adoption of Scheibler's method of two different dilutions overcomes this difficulty. Thus, if R is the rotation when the total volume is V , and r when the volume is v , the equation $V - x/v - x = R/r$ gives x , the volume of the precipitate, and, by subtraction, the real volume of the solution. The conventional method of multiplying by the empirical factor 0.962 gives accurate results with only one particular mixture. The Clerget formula employed by Herzfeld, $Z = 100(P - J)/131.84 - 0.05 J$ is to be preferred to $Z = R - J/1.3266$.
M. J. S.

Source of Error in the Detection of Sugar in Urine by means of Fehling's Solution. By J. EURY (*Bull. Soc. Chim.*, 1900, [iii], **23**, 41—44).—Certain specimens of urine, which are shown by their density and by polarimetric observations to contain notable quantities of sugar, decolorise Fehling's solution when boiled therewith, but yield no precipitate of cuprous oxide. When left to cool, the upper layers of the liquid assume a reddish-brown colour, and a brown precipitate is gradually deposited; this, however, does not take place when the liquid is cooled out of contact with air, nor when the liquid, thus cooled, is afterwards exposed to the air. The reaction is shown to be due to the combination of creatinine and similar bases with cuprous oxide to form soluble compounds, which subsequently undergo oxidation with the precipitation of cupric oxide or a compound thereof with the base. The substances thus interfering with the detection of sugar in urine may be removed by precipitation with mercury, but not with lead salts.
N. L.

Caramel Substances. II. Estimation of Caramel in Aqueous Solutions by means of the Spectroscope. By F. STOLLE (*Chem. Centr.*, 1899, ii, 1099; from *Zeit. Ver. Rübenzuck.-Ind.*, 1899, 839—841).—The method of determining the amount of caramel by means of the spectroscope is based on the property of aqueous solutions of this substance of partially absorbing the rays of the blue end of the spectrum. Caramel is insoluble in absolute ethyl alcohol, but easily

soluble in methyl alcohol, hence it may be readily separated from solutions which contain other active substances. The results obtained are accurate within 0.05 per cent. E. W. W.

Estimation of Cellulose in Fæces. By KONRAD MANN (*Chem. Centr.*, 1899, ii, 1139; from *Arch. Hyg.*, 36, 158—165).—The process recommended by Weender, does not yield a pure cellulose, as this still retains nitrogenous matters, notably elastin. L. DE K.

König's Process for the Estimation of Crude Fibre free from Pentosan. By OSCAR KELLNER, FR. HERING and O. ZAHN (*Chem. Centr.*, 1899, ii, 1033—1034; from *Zeit. Unters. Nahr.-Genussm.*, 2, 784—786).—König's glycerol process (*Abstr.*, 1899, ii, 68) is recommended as being a notable improvement in fodder analysis. L. DE K.

Separation and Estimation of Formic, Acetic, Propionic, and Butyric Acids. By J. SCHÜTZ (*Zeit. anal. Chem.*, 1900, 39, 17—18).—The author is unable to confirm the accuracy of Haberland's method (*Abstr.*, 1899, ii, 531) on the ground that formic, acetic, and butyric acids when evaporated with excess of zinc oxide are not completely converted into their zinc salts, but partially volatilise. The loss increases with increase of the molecular weight of the acid; in one experiment with butyric acid, it amounted to 82 per cent. Similar results were obtained with lead oxide. M. J. S.

Determination of the Solidifying Point of Fatty Acids. By I. FREUNDLICH (*Chem. Zeit.*, 1899, 23, 1014).—This is a slight modification of the Dalican process, consisting in stirring with a delicate thermometer and noticing the sudden rise of the mercury. It is now recommended not to commence the final stirring until the solidifying point is almost reached. L. DE K.

Estimation of Unsaturated Fatty Acids in Fish Oils. By HENRIK BULL (*Chem. Zeit.*, 1899, 23, 1043—1044).—7 grams of the sample are saponified by boiling with 25 c.c. of solution of sodium ethoxide made by dissolving 23 grams of metallic sodium in absolute alcohol and diluting to a litre; the flask containing the mixture is attached to a reflux condenser. When cold, 144.2 c.c. of anhydrous ether are added, the flask stoppered, and frequently shaken for some hours, when the solution is passed through a dry filter, precautions being taken to minimise loss by evaporation. 100 c.c. of the filtrate (= 4 grams of sample) are now shaken thrice in succession with 20 c.c. of water containing a little sodium hydroxide; this treatment removes the sodium salts of the saturated fatty acids, whilst the unsaturated compounds remain in the ethereal liquid. The acids may then be recovered in the usual manner.

A table is given of the analytical data of a large number of marine and fish-oils. L. DE K.

[**Estimation of Calcium Malate in Crude Tartar.**] By CHARLES ORDONNEAU (*Bull. Soc. Chim.*, 1900, [iii], 23, 14—15).—2 grams of the finely powdered tartar are boiled with 100 c.c. of water,

and the liquid filtered, evaporated to about 20 c.c., mixed with 2 c.c. of acetic acid, agitated, and left to cool. The precipitated calcium tartrate is separated by filtration and the filtrate and washings concentrated to about 10 c.c., mixed with 75 c.c. of 93 per cent. alcohol, and the calcium malate thus precipitated collected, washed with alcohol, and dried at 100°. The small quantity of calcium tartrate still mixed with the malate may be estimated by washing the precipitate with water and again drying at 100°. This process, which is based on the properties of calcium tartromalate, may be used for the estimation of malic acid in green grapes, but is not applicable to wines, which contain gummy substances precipitated by alcohol along with the calcium malate. N. L.

Estimation of Uric Acid based on Precipitation as Ammonium Urate. By EMIL WÖRNER (*Zeit. physiol. Chem.*, 1900, 29, 70—77).—The process recommended is a modification of Hopkins' method. The urine is treated with ammonium chloride, the precipitated ammonium urate washed with a saturated solution of ammonium sulphate, and then the nitrogen determined in the precipitate by Kjeldahl's method. Edmund's statement (*Abstr.*, 1895, ii, 237), that ammonium sulphate is a less ready precipitant of the urate than the chloride, is confirmed, in spite of what Folin (*Abstr.*, 1898, ii, 196) says to the contrary. The readiness with which the precipitation occurs with ammonium sulphate increases, however, with rise of temperature. W. D. H.

The Inner Saponification Number. By WILHELM FAHRION (*Zeit. angew. Chem.*, 1899, 1221).—The "inner saponification number" is the figure showing the number of milligrams of potassium hydroxide required to neutralise the non-volatile and non-oxidised fatty acids from 1 gram of fat. The author regards Lewkowitsch's objection to this name and his proposal to call it the "saturation number" as unwarranted. L. DE K.

Constancy in the Composition of Cow's Milk and Detection of its Adulterations. By H. TIMPE (*Chem. Zeit.*, 1899, 23, 1040—1043).—From the results of a large number of analyses, the author concludes that in genuine milk the relation between the proteids and the fat may be expressed by the equation $P = 2 + 0.35 F$.

If the proteids found by actual experiment do not reasonably agree with those obtained by calculation, the milk is either skimmed, watered, or affected both ways. Formulæ are given to facilitate calculation. The question of watering may also be decided from the percentage of milk-sugar found; in fact, the process requires a complete and careful analysis. L. DE K.

Effect of Milk Preservatives on Milk Fat. By BERNHARD SCHULZE (*Bied. Centr.*, 1899, 25, 858; from *Ber. Agri. Versuchs-Stat. Breslau*, 1896).—Small amounts of potassium chromate (0.1—0.2 per cent.) had no essential effect on the amount of milk-fat in 14 days. With more than 0.5 per cent. of chromate there was, however, a considerable reduction in the percentage of fat. Milk which is, perhaps, not

examined for a considerable time should therefore not be treated with uncontrolled quantities of chromate. Salicylic acid seems to be the best preservative. N. H. J. M.

Estimation of Fatty Matter in Butter by Gerber's Process. By J. WERDER (*Chem. Zeit.*, 1899, 23, 1028).—Gerber's acid-butyrometric process gives unsatisfactory results, as a well-defined layer of liquid fat is rarely obtained, but by a slight modification of the method, satisfactory results may be obtained.

1 gram of the sample of butter is treated in the "Gerber butyrometer" (old pattern) with 18 c.c. of sulphuric acid of sp. gr. 1.5 and 1 c.c. of amyl alcohol, and the result multiplied by 1.094; the percentage of fat so found practically agrees with the results obtained by Soxhlet's process. L. DE K.

Bechi and Halphen's Colour Reactions for the Identification of Cotton-seed Oil. By P. N. RAIKOW and N. TSCHERWENIWANOW (*Chem. Zeit.*, 1899, 23, 1025—1028).—The authors, after a lengthy investigation, conclude that the Bechi silver test is quite satisfactory if conducted according to the directions of the Italian Scientific Committee (in which a solution of colza oil in amyl alcohol is used).

The Halphen test, in its original form (heating the sample with sulphur, carbon disulphide, and amyl alcohol), is also an excellent test for the presence of cotton-seed oil in olive and similar oils.

L. DE K.

Macassar Oil. By J. J. A. WIJS (*Zeit. physikal. Chem.*, 1899, 31, 255—257).—The author has determined a number of physical and chemical constants for this oil, and gives a table comparing his values with those of other observers. J. C. P.

Detection of Phytosterol and Cholesterol in Fats. By HANS KREIS and ERNST RUDIN (*Chem. Zeit.*, 1899, 23, 986).—The process recommended by Kreis and Wolf (*Abstr.*, 1898, ii, 343) not being found to be quite satisfactory, has now been modified by the authors as follows: 50 grams of the fat are saponified, as usual, with 125 c.c. of strong alcohol and 25 c.c. of 40 per cent. aqueous caustic potash. When the alcohol has evaporated, the soap is dissolved in 500 c.c. of boiling water, and decomposed by adding 120 c.c. of a 10 per cent. solution of calcium chloride. When cold, the precipitate is collected on a cotton cloth, and the lime-soap pressed dry, powdered, and covered in a closed flask with 100 c.c. of a mixture of equal parts of alcohol and ether. After an hour, the liquid is filtered, and the residue washed with another 50 c.c. of the ethereal mixture; the filtrate is then mixed with 3 c.c. of the aqueous potash and 20 grams of quartz-sand, and evaporated to complete dryness on the water-bath. The residue is extracted with ether in a Soxhlet's apparatus, the solvent evaporated, and the phytosterol, or cholesterol, recrystallised from alcohol. L. DE K.

General and Physical Chemistry.

Rotatory Power of Active Valeric Acid. By PHILIPPE A. GUYE and EMILY ASTON (*Compt. rend.*, 1900, 130, 585—588).—The authors have determined the specific rotatory power of active valeric acid at various temperatures, with the following results:

1st specimen: $[\alpha]_D +11.27$ at 11° , $+10.84$ at 59.5° , $+9.0$ at 188° (vapourised).

2nd specimen: $[\alpha]_D +9.07$ at 16° , $+7.54$ at 99° , $+7.3$ at 188° (vapourised).

In dilute aqueous solution, the acid may be regarded as existing in the form of simple molecules; in a 1.2 per cent. solution, $[\alpha]_D +14.4$ at 18° , and in a 3.9 per cent. solution, $[\alpha]_D +14.6$ at 18° , the rotatory power of the liquid acid being $+12.02$ at 15° . When dissolved in ethylene dibromide, the acid is most probably polymerised; in a 1.27 per cent. solution, $[\alpha]_D +7.8$, in a 2.1 per cent. solution, $[\alpha]_D 9.65$, in an 11.91 per cent. solution, $[\alpha]_D +10.12$, the rotatory power of the liquid acid being $+11.27$ at the same temperature (18°).

The influence of temperature on the specific rotatory power of active valeric acid is not abnormal, and the difference between the acid and the alcohol in this respect is doubtless due to the relatively much smaller effect of temperature in dissociating the acid into simple molecules. It is evident that under ordinary conditions the acid is partially polymerised.

C. H. B.

Silver Germ or Subhaloid Theory. By RICHARD ABEGG (*Chem. Centr.*, 1900, i, 439—440; from *Arch. wiss. Phot.*, 1, 268—272).—An answer to Mercator's objections (*Arch. wiss. Phot.*, 1, 199) to the silver germ theory of the latent photographic image (*ibid.*, 15). Eder's observation (*Phot. Korresp.*, 1899, 233, 276), that collodion plates, even after treating with a very strong nitric acid sensitising bath, still exhibit a faint image on development, shows that a portion of the latent image is destroyed by the acid, and must therefore be due to silver germs. It is still doubtful, however, whether the layer of acid adhering to the plate is sufficient to destroy all the silver germs of the latent image, or whether the image obtained is not due to unattacked germs.

E. W. W.

The Nature of the Latent Image and the so-called Eder Test. By ROBERT LUTHER (*Chem. Centr.*, 1900, i, 440; from *Arch. wiss. Phot.*, 1, 272—274).—When silver powder is repeatedly shaken with fresh quantities of chlorine water, each portion of which contains 1/10th the amount of the chlorine required to convert the silver into chloride, the oxidation potential of the residual chlorine remains constant until just 50 per cent. of the chlorine equivalent to the silver is combined, whilst after this point the oxidation potential increases until the whole of the silver has been converted into chloride. Silver and bromine give similar results, hence the subhaloids, Ag_2Cl and

Ag_2Br , exist, and their formation marks a distinct phase in the action of the halogen on the metal. The oxidation potentials for the conversion of the subchloride and subbromide into the ordinary haloids are 1.15 and 1.45 respectively. When the latent image of a silver bromide plate is treated with a solution of potassium chromate containing hydrogen bromide sufficient to give an oxidation potential of 1.1, the latent image is not attacked, but it is completely destroyed by a solution of oxidation potential 1.2. The oxidation potential of the compound formed by the action of light must therefore be about 1.15, or identical with that of silver subbromide. Similar results were obtained in the case of silver chloride plates, hence, at least in the absence of gelatin, the latent image consists of subhaloids. When silver is placed on a dry plate without pressure, Eder's test fails, and no image is formed on development, but if silver powder, quartz, and silver subbromide are rubbed into a silver bromide gelatin plate, the plate, when developed, shows no change below the quartz, but is black below the silver, and is found to be still more strongly affected under the bromide.

E. W. W.

Electric Charge of the Deviable Rays of Radium. By P. CURIE and SKŁODOWSKA CURIE (*Compt. rend.*, 1900, 130, 647—650).—Those rays emitted by radium which are deviated by a magnetic field are charged with negative electricity, but to a less degree than cathode rays. Hence it may be concluded that the radiation of radium is due to the emission of particles of electrified matter. Röntgen rays are extremely feebly, if at all, charged.

N. L.

[Validity of Maxwell's Equations.] By P. S. WEDELL-WEDELLSBORG (*Zeit. physikal. Chem.*, 1899, 29, 494) and ANTON SCHEYE (*ibid.*, 1900, 32, 145—149).—A continuation of the controversy regarding the validity of Maxwell's equations (see Abstr., 1898, ii, 61, 419.)

L. M. J.

Inversion of Hepta- and Hexa-hydrates of Zinc Sulphate in the Clark Cell. By H. T. BARNES (*J. Physical Chem.*, 1900, 4, 1—20).—The paper contains a more detailed account of the experiments made by the author in conjunction with Callendar on the change of E.M.F. of the Clark cell at a temperature about 39°. The E.M.F. of the cell was determined at various temperatures above 30° by comparison with another maintained at 15°; the experimental details are explained, and curves and tables are given showing the difference between the E.M.F. found and that calculated from the temperature coefficient between 15° and 30°. It is seen that, with ascending temperatures, the change took place at about 42°, and with descending temperatures at about 30°, the curves for the two branches cutting a little below 39°. The variations of E.M.F. with temperature between 0° and 30° in millivolts are given by the expression $E_t - E_{15} = -1.200(t - 15) - 0.0062(t - 15)^2$, and expressions for the two branches above 30° are given, the actual transition point being at 38.78°. The inversion point, as determined by solubility experiments, is 39.95°, but in the Clark cell this temperature must necessarily be lowered by the presence of the mercurous sulphate. The author also considers

that secondary change, due to decomposition of mercurous sulphate, takes place above 35° , as by maintaining a cell at 46° a further change in the E.M.F. was found to occur (Abstr., 1898, ii, 276).

L. M. J.

Potential of the Iodine Electrode. By FRIEDRICH W. KÜSTER and F. CROTOGINO (*Zeit. anorg. Chem.*, 1900, 23, 87—88).—The potential differences between a platinum electrode and various solutions of potassium iodide saturated with iodine have been determined. Solutions have also been used containing different quantities of iodine in a $1/8$ th normal solution of potassium iodide. The results are analogous to those obtained with metal electrodes.

J. C. P.

Potential of Silver in Solutions of its Mixed Halogen Salts. By FRIEDRICH W. KÜSTER and A. THIEL (*Zeit. anorg. Chem.*, 1900, 23, 25—27).—A preliminary note of work arising out of a previous research (Abstr., 1899, ii, 205). The potential between a silver electrode and a normal mixed solution of potassium chloride and bromide, the latter being in equilibrium with a mixed precipitate of silver chloride and bromide, changes gradually from -0.51 volt when there is no silver bromide in the precipitate and no potassium bromide in the solution, to -0.36 volt when there is no silver chloride in the precipitate and no potassium chloride in the solution.

J. C. P.

Three Additions to the Kohlrausch-Ostwald Conductivity Method. By J. LIVINGSTON R. MORGAN (*J. Amer. Chem. Soc.*, 1900, 22, 1—5, 26—28).—Owing to magnetisation of the spring of the contact breaker, the interruptor deteriorates, and the clear note of the telephone is lost. The author describes a form of contact breaker in which this is avoided, the wire conveying the current being attracted by an electro-magnet excited by a separate strong current, this attraction of the wire causing the interruption of the current. Resistances equal to 4, 9, or 19 times that of the metre bridge are so arranged that no readings may be necessary near the end of the bridge; and a double contact key is described, by which two points, about a centimetre apart, are readily obtained, for which the sound intensity is equal, the mid-point giving the zero.

L. M. J.

Influence of Temperature on the Electrical Conductivity of Dilute Amalgams, and the Solubility of Metals in Mercury. By ABSALON LARSEN (*Ann. Phys.*, 1900, [iv], 1, 123—131).—The relative conductivity L_t of liquid amalgams of lead, zinc, cadmium, tin, and bismuth, that is, the conductivity compared with that of mercury at the same temperature, increases proportionally with the temperature, the absolute increase depending on the concentration of the particular amalgam; if $L_t = 1 + \delta_t$, then $\delta_t = \delta_{20}[1 + a(t - 20)]$, the coefficient a varying from 0.0004 for cadmium and zinc amalgams to 0.002 for bismuth amalgams. It appears that in dilute liquid amalgams the dissolved metal is dissociated, and that the degree of dissociation increases both with falling concentration and with rising temperature.

The curve connecting relative conductivity and concentration of the

amalgam shows a break where the limit of solubility is reached. The relative conductivity, and therefore the concentration, of amalgams saturated at various temperatures increases nearly proportionally with the temperature. J. C. P.

Stannic Chloride in Aqueous Solution. By WL. VON KOWALEWSKY (*Zeit. anorg. Chem.*, 1900, 23, 1—24).—The hydrolysis of stannic chloride solutions, according to the equation $\text{SnCl}_4 + 4\text{H}_2\text{O} = \text{Sn}(\text{OH})_4 + 4\text{HCl}$, has been traced by determinations of their conductivity, which increases as time goes on. A point of equilibrium is ultimately reached before hydrolysis is complete, and the effect of a rise of temperature on the equilibrium is to diminish the extent of hydrolysis: the equilibrium in question can further be reached from both sides. Excess

of Cl-ions hinders the hydrolysis, and the conductivity of a mixed solution of stannic chloride and hydrochloric acid may be less than that of the hydrochloric acid solution alone, owing, doubtless, to the formation of a complex salt. Investigation of the freezing points of the solutions, and their influence on the hydrolysis of methyl acetate, leads to the conclusion that the non-electrolytes present interfere considerably with the dissociation of the hydrochloric acid. The author has been unable to determine definitely the concentrations of the various molecules present in solution at the point of equilibrium.

When a solution of stannic chloride is added to a saturated solution of sodium chloride, and the mixed solution is diluted with water, the specific conductivity is found to increase to a certain point with the dilution. J. C. P.

Electrochemical Properties of Silver Fluoride and of Fluorine. By RICHARD ABEGG and CL. IMMERWAHR (*Zeit. physikal. Chem.*, 1900, 32, 142—144).—The conductivity of solutions of silver fluoride at dilutions of from about $N/1$ to $N/200$ was determined, and from the values the dissociation was calculated; at the higher concentrations, this is approximately equal to that of silver nitrate. In the more dilute solutions, high values for the conductivity indicate partial hydrolysis of the salt. The decomposition tension of fluorine exceeds that of chlorine by about 0.45 volt, and it is noticeable that an approximately equal difference separates the other halogens. An increase of solubility of silver oxide is occasioned by addition of silver fluoride, this being probably due to the formation of complex ions.

L. M. J.

Electrochemical Equivalent of Copper and Silver. By THEODORE W. RICHARDS, EDWARD COLLINS, and GEORGE W. HEIMROD (*Zeit. physikal. Chem.*, 1900, 32, 321—347).—An examination of the irregularities of the copper voltameter leads in general to results agreeing with those of Foerster and Seidel (compare Abstr., 1897, ii, 241; 1898, ii, 10). Copper plates become lighter in acidified copper sulphate solutions, owing to the solution of the copper and the simultaneous formation of cuprous sulphate: this action increases as the temperature rises. Copper plates in neutral copper sulphate solutions become heavier by the deposition of cuprous oxide, formed by the hydrolysis of cuprous sulphate. With regard to the copper

voltameter, the authors point out that (1) the solution must be as cold as possible; (2) the solution must be acid to prevent hydrolysis; (3) the solution must be as dilute as possible, whilst the liberation of hydrogen is avoided; (4) air must be carefully excluded. Foerster and Seidel's plan of saturating the solution from the beginning with cuprous ions is criticised as giving too heavy a deposit of copper: this view is borne out by experiment. Comparison of the copper deficit in the copper voltameter with the current density at the cathode shows: (1) that a high current density gives far too low a deposit of copper, owing doubtless to the separation of hydrogen; (2) that the loss of copper due to solution in the copper sulphate is approximately proportional to the extent of the electrode surface. By taking then the actual weight of copper deposited in any given case, and extrapolating to the electrode surface zero, a value is obtained which will correspond closely with the amount of electricity that has passed through the cell. A series of experiments, treated in this way and based on a comparison of the copper voltameter with the ordinary silver voltameter, gave the mean value 63.563 for the atomic weight of copper, distinctly less than the value 63.604, obtained by purely chemical methods.

As regards the silver voltameter, it appears from the work of numerous observers that some substance, connected with or proceeding from, the anode, causes too large a deposit of silver at the cathode. Experiment having shown that the cathode deposit was not contaminated by mother liquor, the authors adopted the device of inserting a porous cell between the anode and the cathode. This arrangement of the silver voltameter gives, under similar conditions, a smaller deposit of silver than any other of the forms used. The quantity of silver deposit is less affected by change of temperature in this porous cell form of the voltameter than in Lord Rayleigh's form, and the authors consider their results the more correct. When the necessary correction is made on the ordinary silver voltameter, the atomic weight of copper, deduced from the experiments described above, now lies between 63.598 and 63.615. The electrochemical equivalent of silver is corrected to 0.0011172 gram per amp. sec., and that of copper to 0.0003292 gram per amp. sec. J. C. P.

Electrochemical Equivalent of Carbon. By H. C. PEASE (*J. Physical Chem.*, 1900, 38—40).—The electrochemical equivalent of carbon was found by determining the loss of weight of a carbon anode in fused caustic potash, iron being used for the cathode. The results obtained were 3.15, 3.66, 3.40, 3.23 and 3.14, which, when a slight loss due to disintegration is allowed for, indicated the electrochemical equivalent of 3 (Abstr., 1893, ii, 14). L. M. J.

The Electrical Reduction of Non-electrolytes. By FRITZ HABER (*Zeit. physikal. Chem.*, 1900, 32, 193—270).—For the electrolytic reduction of nitrobenzene in alkaline solution, the equation is deduced: $\epsilon = 0.0436 \log(I/C_{NO_2}) - \text{const.}$, where ϵ is the fall of potential at the cathode, I the current strength, and C_{NO_2} the concentration of the nitrobenzene in the cathode solution. This equation, which holds for ordinary temperatures, is based on Nernst's formula for the fall of

potential at an electrode, on the law of mass action, and on the conception of the cathode as a solid solution of the reducing agent. In three series of experiments, where the fall of potential, the concentration of the nitrobenzene, and the current strength respectively were kept constant, the equation just given was found to agree with the results of observation. A plain platinum cathode was used in almost all cases. The equation $\epsilon = 0.0436 \log(10/C_{No_2}) - \text{const.}$, represents the results satisfactorily both with a platinised platinum cathode in alkaline solution and with a plain platinum cathode in acid solution. J. C. P.

Recent Researches on Magnetic Susceptibility. By JOH. KÖNIGSBERGER (*Ann. Phys.*, 1900, [iv], 1, 175—177).—A criticism of some of Meyer's results and conclusions (this vol., ii, 7). The author holds that compounds of two diamagnetic elements may be paramagnetic. In the case of certain compounds for which Meyer observed no influence of the field strength, such an influence has been detected. J. C. P.

Thermochemical Law of Maximum Work. By ALBERT REYCHLER (*Chem. Centr.*, 1900, i, 162; from *Rev. Univ. Bruxelles*, 1899, 5, 5—16).—The author shows that, under certain conditions, Berthelot's law of maximum work can be looked on as a consequence of the fundamental laws of thermodynamics. Superheated systems are those which are in equilibrium at a lower temperature, supercooled those which were in equilibrium at a higher temperature; the former are endothermic, the latter exothermic. Non-reversible reactions take place in supercooled systems, and are always exothermic; reversible reactions are only exothermic when the temperature is below that of equilibrium. Berthelot's law should be interpreted as meaning that heat is developed by all spontaneous changes in systems which are below their temperature of equilibrium. Supercooled systems may be due to the fact that during the process of cooling, external causes prevented equilibrium being established at each temperature; thus sulphur and free oxygen exist together on the earth. Exothermic, and therefore supercooled, systems may also arise through access of energy by radiation, although the temperature of equilibrium did not prevail at the point of formation. J. C. P.

Tubular Furnace giving Fixed Temperatures, adjustable at Will. By ARMAND GAUTIER (*Compt. rend.*, 1900, 130, 628—633).—A detailed description of a form of gas furnace by means of which any desired temperature between 150° and 1300° may be maintained constant within a few degrees for several hours. The apparatus consists essentially of an iron tube containing the glass or porcelain tube to be heated and enclosed in a fire-clay casing, between which and the iron tube pass the flames of two rows of Bunsen burners supplied with gas at a carefully regulated pressure. N. L.

Measurement of Low Temperatures. II. By ALBERT LADENBURG and C. KRÜGEL (*Ber.*, 1900, 33, 637—638. Compare Abstr., 1899, ii, 545).—More careful measurements than those already carried out (*loc. cit.*) lead to the following revised data. *Boiling points:*

Oxygen, -182.2° (745.0 mm.); nitric oxide, -142.8° (757.2 mm.); hydrogen chloride, -83.1° (755.4 mm.); hydrogen bromide, -68.1° (755.4 mm.); hydrogen iodide, -36.7° (751.7 mm.); hydrogen sulphide, -60.4° (755.2 mm.); methane, -162° (751.0 mm.); ethane, -84.1° (749.0 mm.); propylene, -48.2° (749.0 mm.); trimethylene, about -34° (749.0 mm.); acetylene, -82.4° .

Melting points: Nitric oxide, -150.5° ; ammonia, -75.5° ; hydrogen chloride, -111.3° ; hydrogen bromide, -86.13° ; hydrogen iodide, -51.3° ; hydrogen sulphide, -82.9° ; ethane, -172.1° ; trimethylene, -126.6° ; toluene, -93.2° ; ethylbenzene, -93.2° ; mesitylene about -57.5° ; cymene, -73.5° ; methyl chloride, -102.9° ; ethyl bromide, -115.8° ; ethyl iodide, -110.6° to -113.1° ; methyl alcohol, -93.9° ; ethyl alcohol, -111.8° ; ethyl ether, -113.1° ; acetaldehyde, -120.6° ; acetone, -93.9° ; ethylene glycol, -15.6° ; methyl formate, -100.4° ; ethyl acetate, -82.4° ; ethylamine, -83.8° . T. H. P.

Specific Heat of Metals at Low Temperatures. By U. BEHN (*Ann. Phys. Chem.*, 1898, [ii], 66, 237—244).—Small cylinders of aluminium, iron, nickel, copper, lead, palladium, iridium, and platinum, contained in test-tubes, were cooled in a bath of liquid air or a mixture of solid carbon dioxide and alcohol; they were then introduced into a quantity of water in a calorimeter, and the specific heat calculated in the usual way. In all cases examined, the specific heat diminishes as the temperature falls, the decrease being greatest for the metals with large specific heat. The mean atomic heats of copper, nickel, iron, and aluminium, in the interval -79° to -186° , lie between the values 4.0 and 4.5. J. C. P.

Specific Heat of Metals, Graphite, and a few Alloys at Low Temperatures. By U. BEHN (*Ann. Phys.*, 1900, [iv], 1, 257—269).—The specific heats of antimony, tin, cadmium, silver, zinc, magnesium, and graphite have been determined by the method and at the temperatures formerly employed (see preceding abstract). In these, as in the earlier cases, the specific heat diminishes with falling temperature; the smaller the atomic weight of the metal, and the lower the temperature reached, the greater is the decrease of the specific heat. The mean atomic heat of graphite for the interval -79° to -186° is only 0.9.

From the mean specific heats obtained by experiment, the true specific heat c at any particular temperature t may be calculated, with the help of the relation $c = A + Bt + Ct^2$, where A , B , and C are constants. The atomic heat of graphite at -186° is thus calculated to be 0.486. Of the curves showing the relation between true specific heat and temperature, those for lead, antimony, tin, and graphite are nearly straight lines. The variation of specific heat with temperature is seen from these curves to be greatest in the case of elements with a small atomic weight and a small atomic volume.

For brass and a few alloys of lead and tin, the specific heat has approximately the same value as that calculated from the specific heats of the component metals. J. C. P.

Method for the Determination of the Melting Point. By MITSURU KUHARA and MASUMI CHIKASHIGÉ (*Chem. News*, 1899, **80**, 270—271).—Instead of being placed in a capillary tube, a thin layer of the substance is held between two pieces of thin glass (microscope cover glasses) and suspended by a platinum foil support in a test-tube, which is placed in the sulphuric acid bath.

D. A. L.

Regularities in Melting Points. By THEODOR SALZER (*J. pr. Chem.*, 1900, [ii], **61**, 165—168).—The regular fall of melting point in the series of alkylsuccinic acids has been confirmed by Bone and Sprankling's determination of the melting point of methylsuccinic acid (*Trans.*, 1899, **75**, 839).

In the malonic acid series, a similar regularity cannot be observed, since the decomposition points are very low. Thus malonic acid and methylethylmalonic acid were found to decompose at the melting point, and isopropylmalonic acid at 120°, but dimethylmalonic acid is stable at the melting point.

Further regularities occur in the melting points of the following series: (1) Acetanilide (112°), propionylanilide (105°), butyrylanilide (90°); (2) methyl, ethyl, and propyl *p*-hydroxybenzoates (131°, 112·5° or 116°, and 96°); (3) the aurichlorides of morpholine, methylmorpholine, and ethylmorpholine (240°, 183°, and 125°); (4) α -methylpiperidine, α -ethylpiperidine, and α -propylpiperidine (167°, 121°, and 85°); (5) β -methylpiperidine, β -ethylpiperidine, and β -propylpiperidine (139°, 112° or 108°, and 98° or 93°).

T. M. L.

Heat of Sublimation of Carbon Dioxide, and Heat of Vaporisation of Air. By U. BEHN (*Ann. Phys.*, 1900, [iv], **1**, 270—274).—The mean specific heat of a metal being known for the interval 18° to -183° (see preceding page), it is possible, by dropping a cylinder of the metal into liquid air and measuring the quantity of vapour formed, to calculate the heat of vaporisation of air; the value actually found as a mean of two experiments was 50·8 Cal. An analogous process for solid carbon dioxide in absolute alcohol gave for the heat of sublimation of carbon dioxide the value 142·4 Cal., the two separate experimental results being 142·0 and 142·8 Cal.

When these values for r , the heat of sublimation or vaporisation, are introduced in the equation $Jr = T.s.dP/dT$, where J is the mechanical equivalent of heat, T the absolute temperature, s the specific volume of the vapour, and dP/dT the temperature coefficient of the vapour pressure, the specific volume of gaseous air at -183° is calculated to be 358, and that of gaseous carbon dioxide at -79° to be 423.

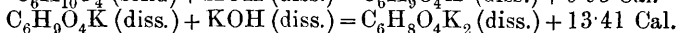
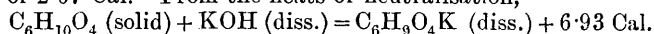
J. C. P.

Heat of Neutralisation and Electrolytic Dissociation. By A. THIEL (*J. pr. Chem.*, 1900, [ii], **61**, 141—150).—A criticism of Vaubel's conclusions as to the significance of the thermochemical data for the heat of neutralisation of acids and bases (*Abstr.*, 1899, ii, 727).

T. M. L.

Thermochemistry of Normal Adipic Acid. By GUSTAVE MASSOL (*Bull. Soc. Chim.*, 1900, [iii], **23**, 100—101).—Anhydrous

normal adipic acid melts at 146.5° (Arppe gives 148° , and Bromeis 145°); its solubility in water (1 per cent. at 15°) is too small to allow its heat of dissolution to be determined. Normal potassium adipate becomes anhydrous at 100° , and dissolves in water with the development of 2.67 Cal. From the heats of neutralisation,



it is calculated that the heat of formation of normal potassium adipate is 45.45 Cal., all the substances concerned being in the solid state. Adipic acid is therefore perfectly comparable with its homologues, succinic, glutaric, and suberic acids, for which the corresponding figures are 46.50 Cal., 44.23 Cal., and 44.76 Cal. respectively (Abstr., 1899, ii, 80). N. L.

Isomerism of Thiocyanic Derivatives. By MARCELLIN P. E. BERTHELOT (*Compt. rend.*, 1900, 130, 441–447).—A thermochemical study of the isomeric thiocyanates and thiocarbimides. The following constants are recorded :

	Heats of combustion.		Heat of formation.	Heat of transformation of normal- into iso-salt.
	Constant volume.	Constant pressure.		
Methylthiocyanate.....	452.1 Cal.	453.1 Cal.	-19.9 Cal.	8 to 9 Cal.
Methylthiocarbimide (solid)	441.6 „	442.6 „	-9.4 „	—
Ethylthiocyanate.....	612.5 „	613.8 „	-17.25 „	9.6 „
Ethylthiocarbimide	602.8 „	604.1 „	-7.6 „	—
Phenylthiocarbimide	1019.0 „	1020.3 „	-46.5 „	—
Allylthiocarbimide.....	731.2 „	732.6 „	-41.8 „	—
Thiosinamine.....	790.4 „	781.8 „	-6.48 „	—

G. T. M.

Meconin, Opianic and Hemipinic Acids. By ÉMILE LEROY (*Compt. rend.*, 1900, 130, 508–510).—The heat of combustion of meconin at constant volume is 1136.2 Cal., and, at constant pressure, 1136.5 Cal., its heat of formation being 151.6 Cal.; this substance, considered as a dimethoxyphthalide, is comparable with phthalide; their heats of combustion differ by 251.1 Cal., and a similar difference exists between those of benzene and its methoxy-derivatives. When meconin is oxidised to opianic acid, the heat developed is 46.1 Cal., the mean value for the heat of oxidation of an alcohol to an aldehyde is greater than 50 Cal.; the discrepancy is probably due to the slight thermal change which accompanies the dehydration of the hydroxy-acid, of which meconin is the inner anhydride. The heats of combustion, formation, and dissolution of opianic acid are 1090.4, 197.7, and -6.8 Cal. respectively; the heat of neutralisation of the dissolved acid by a solution of potassium hydroxide is 15.53 Cal. Opianic acid almost completely displaces acetic acid, the heat developed being 2.0 Cal., the value calculated for complete displacement being 2.2 Cal. The heat of dissolution of crystallised potassium opianate, $\text{C}_{10}\text{H}_9\text{KO}_5, 2\frac{1}{2}\text{H}_2\text{O}$, is -4.88 Cal., whilst that of the salt dehydrated at low temperatures is 4.30 Cal.; when dried at higher temperatures, the heat developed is only 1.20 Cal.; the heat of formation of the solid salt is 18.44 Cal. The two isomeric methyl opianates have

practically the same heats of combustion and formation, the mean values of these constants being 1262 Cal. and 189.7 Cal. respectively. The heat of combustion of hemipinic acid is 1024.7 Cal., and its heat of formation 263.5 Cal.

The difference between the heats of combustion of hemipinic and phthalic acids is 253 Cal., and corresponds with the thermal change produced by the introduction of two methoxyl groups into the molecule of the latter compound; this supports the view that the former acid is a dimethoxyphthalic acid.

The heat of oxidation of opianic acid to hemipinic acid agrees closely with the normal value of the thermal change produced by the oxidation of an aldehyde to an acid. The heat of oxidation of meconin to hemipinic acid is 111.0 Cal., whilst that of phthalide to phthalic acid is 113.8 Cal.

G. T. M.

Freezing Point Method in Dilute Solutions, and the Theory of Solutions. By MEYER WILDERMANN (*Zeit. physikal. Chem.*, 1900, 32, 288—302).—A review of recent work on this subject, and a criticism in particular of Dieterici's views and results (*Abstr.*, 1898, ii, 207; 1899, ii, 403).

J. C. P.

Abnormal Depressions of the Freezing Point produced by Chlorides and Bromides of the Alkaline Earths. By HARRY C. JONES and VICTOR J. CHAMBERS (*Amer. Chem. J.*, 1900, 23, 89—105).—The depression of the freezing point produced by the chlorides and bromides of calcium, strontium, barium, and magnesium in aqueous solutions of various concentrations has been measured; unlike the alkali halogen salts, which produce a continually increasing molecular depression with increase of dilution, the salts of the alkaline earths give rise initially to a *decrease* of the depression, which falls to a minimum at a concentration between $N/10$ and $N/5$, but subsequently increases in the ordinary manner with increasing dilution. With cadmium chloride or bromide, however, normal results are obtained, the molecular depression increasing regularly with increase of dilution. A comparison of the electrical conductivities of the salts named, in solutions of varying concentration, shows no irregularity in the region where the molecular depression is a minimum. Since the halogen salts of the alkaline earths are very hygroscopic, it is suggested tentatively, as a possible explanation of their abnormal behaviour, that in concentrated solutions they combine with a portion of the water used as solvent, forming complex hydrates, which undergo dissociation on increasing the dilution. The conductivity results, which show that marked dissociation occurs in the concentrated solutions, cannot, however, be readily reconciled with this view unless it is assumed that a certain number of the molecules are ionised by the water in combination with them just as salts are probably dissociated by their water of crystallisation.

W. A. D.

Cryoscopic Observations. By KARL AUWERS [and, in part, W. BARTSCH, F. H. BETTERIDGE, MAX DOHRN, and H. M. SMITH]. (*Zeit. physikal. Chem.*, 1900, 32, 39—62).—Various derivatives of *p*-cresol which are *o*-hydroxy-ketones were found to be cryoscopically

normal in naphthalene solution; *p*-nitrobenzoyl-*p*-cresol, however, yields a curve which falls with increasing concentration, no explanation of this anomaly being assigned. *p*-Hydroxy-ketones of the type of *p*-hydroxyacetophenone were found to yield abnormal curves, the abnormality increasing with molecular weight, a result which differs from that usually obtained in such cases. Methyl *p*-hydroxybenzoate is abnormal, but the halogen derivatives ($\text{OH} : \text{Cl} = 1 : 2$) are all almost normal, the halogens having approximately equal normalising influence. A number of derivatives of *p*-hydroxybenzaldehyde were found to be abnormal, but to a less extent than the parent substance. Amongst the diphenols and their monomethoxy-derivatives, resorcinol was found to be abnormal, guaiacol normal, and the remainder slightly abnormal. Dimethyl oxalate was also employed as a solvent, and it was found that compounds cryoscopically abnormal in naphthalene give almost normal results, so that the solvent is only weakly abnormalising. *p*-Azoxyanisole was also used as a solvent, all the compounds investigated giving normal curves; the cryoscopic constant of this solvent is, however, somewhat uncertain; Schenck adopted the value 750, whilst the author obtains a mean value of 545, with, however, very wide limits, so that before the compound is useful cryoscopically, this uncertainty must be removed (Abstr., 1899, ii, 637). L. M. J.

Corresponding States. By KIRSTINE MEYER née BJERRUM (*Zeit. physikal. Chem.*, 1900, 32, 1—38).—Although van der Waals's expression can be only regarded as an approximation, nevertheless the important law of corresponding states may be valid, and the paper contains an elaborate investigation of known data in order to determine whether this is the case or not. If a law of corresponding states holds, then, assuming the critical states as corresponding for any pair of compounds, at corresponding temperatures T and T' the expression $\log.(T_c - T) - \log.(T'_c - T')$ is constant and independent of pressure, whilst a similar expression $\log.(P_c - P) - \log.(P'_c - P')$ is independent of temperature. Curves for $\log.(T_c - T)$ against $\log.(P_c - P)$ for the two compounds should therefore by mere displacement be superposable, and this is found to be the case, whilst, further, since $\log.(P_c - P) - \log.(P'_c - P') = \log.P_c - \log.P'_c$, it follows that equal fractions of the critical pressure are corresponding pressures. This, however, does not hold for temperature, that is corresponding temperatures, at which the vapour pressures are equal fractions of the critical pressure, are not always equal fractions of the critical temperatures, and for comparison temperatures must be measured from different zero values, usually a few degrees above 273° . This is also the case for volumes, the ratio of corresponding volumes not being that of the critical volumes, but equal to a ratio q/q' , where q' is usually slightly greater than the critical volume. The law of corresponding states hence does actually obtain, but temperatures and volumes must be measured from different null points. The validity of the deductions is also proved by the comparison of the found and calculated isothermals of isopentane, hexane, ether, and carbon dioxide. Water and the alcohols form exceptions to these deductions, and this is probably to be ascribed to molecular association. L. M. J.

Absolute Molecular Volumes. By CATO M. GULDBERG (*Zeit. physikal. Chem.*, 1900, 32, 116—126).—By extreme compression of a liquid, a value may be assumed to be finally reached which is the absolute volume of the molecules, and is independent of temperature; whilst, similarly, the same value, independent of pressure, is reached by cooling to the absolute zero. Assuming the validity of the expression $p/RT = 1/(v - v_0) - \alpha$, then the value for v_0/v may be obtained by comparison of the volumes at either two temperatures or two pressures. These, however, involve the unknown constant, α , but by neglecting the term in which it occurs, the ratios are in one case too great, and in the other too small, and the values, which do not greatly differ, are given for a number of different compounds, the compressibility data being obtained from Amagat's results. The author has also given an empirical expansion law, which may be expressed as $\alpha = \alpha_0/\sqrt{1-t}$, where t is the ratio of the absolute temperature to a certain temperature T , which varies for different liquids, but is for many equal to the critical temperature. De Heen has also given the expression $\alpha = \alpha_0/(1 - \frac{4}{3}\alpha_0 T)$, and from each of these expressions v_0/v is calculable. From these, the values v_0 are derived, and it is seen that the numbers agree well with the previous values. The absolute molecular volumes and densities are so calculated and given for about 80 liquids. The mean value of the ratio of the critical volume to the absolute molecular volume is found to be 3.75. This absolute molecular volume is, however, not the sum of the atomic volumes, being dependent on structure; thus carbon, which has in the diamond an atomic volume of 3.4, has in organic liquids an atomic volume of 7.2. The molecular volumes so obtained may be approximately expressed by assuming $C = O = N = 1$; $H = \frac{1}{2}$; $Cl = P = As = S = Si = 2.5$; $Br = 3$; $I = 3.75$, the unit varying in different classes of compound between 7.1 and 7.9, and being greatest for unsaturated compounds. L. M. J.

Development and Application of a General Equation for Free Energy and Physico-chemical Equilibrium. By GILBERT NEWTON LEWIS (*Zeit. physikal. Chem.*, 1900, 32, 364—400).—A theoretical paper not suitable for abstraction. J. C. P.

Chemical Affinity. By WILHELM VAUBEL (*Chem. Zeit.*, 1900, 24, 35—36).—The author regards chemical affinity as made up of two components—gravito-affinity and electro-affinity. The part played by each of these factors is illustrated by several numerical examples, based on the author's previous papers (Abstr., 1898, ii, 206 and 503; 1899, ii, 727). J. C. P.

Diazotisation and the Affinity Constants of Nitrous Acid. By M. SCHÜMANN (*Ber.*, 1900, 33, 527—533).—The author has studied the velocity of the change represented by the equation $R \cdot NH_3Cl + HNO_2 \rightarrow R \cdot N_2Cl + 2H_2O$, by observing the fall of electrical conductivity in aqueous solution due to the transformation of the original disassociated acid system into the neutral, non-dissociating diazonium chloride; this method is possible, because all diazonium chlorides show practically the same conductivity in solution, and is superior to that employed by Hantzsch and Schümann (Abstr., 1899, ii, 549), in that its rapidity

enables the first phases of the process to be accurately observed. The conclusion finally arrived at is that, in presence of an excess of acid, and in absence of secondary decomposition, "all aromatic amines are diazotised at approximately the same speed."

The experiments were carried out at 20°, by adding an *N*/500 solution of sodium nitrite to an *N*/500 solution of the hydrochloride of the base containing 1 mol. of hydrochloric acid. With *p*-anisidine and *p*-toluidine, the conductivity falls regularly, until a constant final value is reached after 2 hours; with aniline, *o*-toluidine, and ψ -cumidine, however, the minimum value, which is reached after about 2 hours, does not remain constant, but subsequently increases, owing to the secondary change, $R \cdot N_2Cl + H_2O = R \cdot OH + HCl + N_2$, occurring. In some cases, the formation of a diazoamino-compound introduces a similar disturbing influence; with *p*-bromoaniline, this factor produces little effect (compare Hantzsch and Schumann, *loc. cit.*), but with α - and β -naphthylamine, considerable quantities of diazoamino-compounds are formed in the first few minutes.

The author has also determined the affinity-constant of nitrous acid by measuring the conductivity of aqueous solutions of carefully purified sodium nitrite; for $NaNO_2$ at 25°, $\mu_\infty = 115.5$, and hence for HNO_2 at 25°, $\mu_\infty = 391.5$, and therefore $K = 0.045$. This value indicates that in the diazotisation process a considerable repression of the hydrolytic dissociation of the salt of the aromatic base must be caused by the nitrous acid; hence it is impossible to calculate the conductivity of the system additively from that of its components. W. A. D.

Chemical Equilibrium in a System of Four Gases. By H. PÉLABON (*Compt. rend.*, 1900, 130, 576—579).—The action of hydrogen on mercury selenide above 500° provides a case of four gaseous substances which, at a given temperature, are in chemical equilibrium; and the author shows that through a fairly wide range of pressure, and even in presence of excess of mercury, the partial pressures observed agree with those deduced from mechanical and thermochemical principles. C. H. B.

Relations between Ammonia and Salts in Aqueous Solution. By DMITRI P. KONOWALOFF (*J. Russ. Phys. Chem. Soc.*, 1899, 31, 910—927).—The relations between the strength of an aqueous ammonia solution and the pressure exerted by the ammonia in the solution have been determined at 59.96°. In the following table, *n* represents the number of gram-mols. of ammonia per litre, and *P* the partial pressure in mm. of mercury, due to the ammonia dissolved:

<i>n</i>	3.098	1.549	1.239	1.033	0.7745	0.6196
<i>P</i> ₁	202.0	94.01	74.42	61.4	45.66	36.39
<i>P</i> ₁ / <i>n</i>	65.3	60.7	60.0	59.4	58.9	58.7

The presence of dissolved salts causes a diminution in the value of *P*₁ and for solutions containing less than about 1.5 gram-mols. of ammonia per litre (for which Henry's law is approximately true), this diminution is expressed by the following formula: $P = P_1(n - km)$, where *P*₁ represents the pressure of the ammonia in pure aqueous solution, *P* the pressure of the dissolved salt, *n* and *m* the number of

gram-mols. of ammonia and salt respectively in a litre of the solution, and k a constant. For silver nitrate, $k=2$, whilst for cadmium nitrate, zinc nitrate, nickel chloride, copper nitrate, copper chloride, copper sulphate, and copper acetate, k approximates more or less closely to the value 4. The more stable a solution is towards water, so much the more nearly do the values of k approach 4, the deviations from this number being greatest for those solutions which most readily give a precipitate on the addition of water. These facts are explained as due to the formation in solution of compounds $\text{MX}_2 \cdot 2\text{NH}_3$ (in the case of silver nitrate), or $\text{MX}_2 \cdot 4\text{NH}_3$ (for the salts of dibasic acids). Support is given to this hypothesis by the fact that increasing quantities of copper sulphate, when dissolved in aqueous ammonia, cause increasing elevations of the freezing-point, the magnitudes of the elevations being the same as would be produced if the compound $\text{CuSO}_4 \cdot 4\text{NH}_3$ were formed in the solution.

The colour of aqueous salt solutions is regarded as due to the existence of definite hydrates in the solutions, the different colours obtained in the presence of ammonia being caused by the formation of compounds of the salt with ammonia analogous to the hydrates. The change in electrical conductivity of a solution of ammonia on adding copper salts and that produced in a nickel sulphate solution by the addition of ammonia, are also explained by the formation of such compounds.

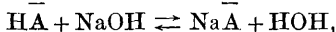
When ammonia combines with a salt, it causes a large increase in its electrical conductivity, whilst the replacement of the combined ammonia by water is accompanied by comparatively small changes in the conductivity. Thus luteocobaltic bromide, $\text{CoBr}_3 \cdot 6\text{NH}_3$, at a dilution of 500 litres, has the molecular conductivity, 401.6; $\text{CoBr}_3 \cdot 5\text{NH}_3 \cdot \text{H}_2\text{O}$ gives the value 390.3; $\text{CoBr}_3 \cdot 4\text{NH}_3 \cdot 2\text{H}_2\text{O}$, 379.8; $\text{CoBr}_3 \cdot 5\text{NH}_3$, 244.7; and $\text{CoBr}_3 \cdot 4\text{NH}_3$, about 190.6. T. H. P.

Equilibrium in Systems containing an Alkali Salt, Water, and Alcohol. By B. R. DE BRUYN (*Zeit. physikal. Chem.*, 1900, 32, 63—115).—The following systems were examined, water, ethyl alcohol, and (1) ammonium sulphate, (2) potassium carbonate, (3) sodium sulphate, and water, methyl alcohol, potassium carbonate. These differ from the systems examined by Schreinemakers, inasmuch as no pair forms two liquid phases. The systems containing the sulphates were most fully investigated, and for these spacial diagrams are given. In the system, ammonium sulphate—alcohol—water, a lower critical point occurs, about 8° , below which no separation into liquid phases can occur. Increase of temperature causes an increase of solubility in dilute alcohol, and the binodal curve indicates that for a high percentage of alcohol, cooling of a homogeneous solution causes a separation into two layers, whilst for solutions of low percentage the reverse obtains. The system, potassium carbonate—water—ethyl alcohol, gave no critical point between 75° and -18° ; as in the previous case, in systems of small alcohol content, warming causes a separation into two layers, and at certain compositions further increase of temperature again produces homogeneity. At all temperatures, potassium carbonate has a much greater effect than ammonium

sulphate in this respect. The hydrates were found to have the composition $K_2CO_3 \cdot 3H_2O$ and $K_2CO_3 \cdot 2H_2O$ respectively. In the system with methyl alcohol, a lower critical point of -35° was found, and at all temperatures in the presence of the solid hydrated carbonate, methyl alcohol and water are more miscible than water and ethyl alcohol. In systems of sodium sulphate—water—ethyl alcohol, above 32.5° , the anhydrous is the only solid phase; below this temperature, either the anhydrous salt or the decahydrate may occur; solutions in equilibrium with the heptahydrate are not stable. The solubility of the hydrates in dilute alcohol increases with temperature, that of the anhydrous salt decreases. Systems with two layers were obtained, but are unstable below 32.5° , and at 25° speedily deposit crystals of the hydrate with the formation of but one liquid phase. In this system, the complete spacial diagram between 0° and 45° is given.

L. M. J.

A Case of Chemical Equilibrium suitable for Demonstration. By PAUL DUDEN (*Ber.*, 1900, **33**, 483—484).—Benzenesulphoncamphylamide is suspended in an excess of 10 per cent. sodium hydroxide solution, and, in the course of half a minute, is converted almost completely into the insoluble sodium salt; on adding ether, almost the whole of the sulphonamide is regenerated. In this way, it is easy to demonstrate the fact that in the equation



the equilibrium passes over almost completely to the right or to the left when the sodium salt or the acid is removed from the liquid phase in which interaction takes place. Benzenesulphoncamphenamide can also be used with a 6—7 per cent. solution of sodium hydroxide.

T. M. L.

Solubility of Carbon Dioxide in Alcohol between -67° and $+45^\circ$. Invasion and Evasion Coefficients at 0° . By CHRISTIAN BOHR (*Ann. Phys.*, 1900, [iv], **1**, 244—256. Compare Abstr., 1898, ii, 211, and 1899, ii, 641).—Two methods have been employed, one consisting in saturating the alcohol with carbon dioxide, and subsequently determining the quantity of gas absorbed, the other being an ordinary absorption method, and used at temperatures below 0° . The formula $\alpha(T-n) = K$ (Abstr., 1898, ii, 211) is found applicable, the variation of n between -12° and 36° being very small. The values of α obtained at ordinary temperatures agree well with those of Carius; at 0° , α has the value 4.3, and as the temperature falls, it increases to about 44 at -67° . At the lowest temperatures, however, the absorption of gas causes considerable alteration of volume, and there is a little uncertainty about the extent of the correction to be applied.

The quantity b , given by the equation $b = (\log x_0 - \log x) / t \cdot \log e$ (Abstr., 1899, ii, 641), is satisfactorily constant, and the evasion coefficient at 0° is thence calculated to be 0.524. From the relation $\gamma = \alpha\beta$, where α is the absorption coefficient, β the evasion coefficient, and γ the invasion coefficient, γ is calculated to have the value 2.375

at 0°; direct experiment gave the value 2.459. The following table gives the various coefficients for water and alcohol:

	β	γ	α
Water	0.077	0.132	1.713
Alcohol	0.524	2.375	4.532

J. C. P.

Relation between the Dissociation Constant of Weak Acids and the Hydrolysis of their Alkaline Salts. By JAMES WALKER (*Zeit. physikal. Chem.*, 1900, 32, 137—141).—The author has recently determined the dissociation constants of a number of weak inorganic acids (Walker and Cormack, *Trans.*, 1900, 77, 5). From these results, the values of the hydrolysis of the sodium salts may be calculated by the expression $x^2/(1-x)v = k^2/c$, where x is the quantity of salt hydrolysed, and k and c are respectively the dissociation constants of water and the acid. By the reverse calculation, van Laar obtained values for the dissociation of hydrocyanic acid and phenol considerably higher than the experimental determinations of the author, but this was due to the use of an erroneous high value for the dissociation of water (*Abstr.*, 1894, ii, 132). The following values are obtained for the percentage hydrolysis of the sodium salts in $N/10$ solutions: Acetate, 0.008; bicarbonate, 0.06; hydrosulphide, 0.14; metaborate, 0.84; cyanide, 0.96; phenoxide, 3.0; these agree satisfactorily with the direct determinations of Shields (*Abstr.*, 1893, ii, 418), acetate, 0.008; borax, 0.5; cyanide, 1.1; phenoxide, 3.0. The hydrolysis of sodium phenoxide calculated by the author is also in accord with the direct determinations of Hantzsch, although the determinations of the conductivity made by the latter do not agree with the author's results (*this vol.*, i, 94).

L. M. J.

Hydrolysis of Salt Solutions. By LUDWIK BRUNER (*Zeit. physikal. Chem.*, 1900, 32, 133—136).—Results are communicated of work on the same lines as that of Ley (*this vol.*, ii, 67) on the hydrolytic dissociation of salts. The method of sugar inversion was employed for the measurement of the dissociation, and the following results were obtained. The chlorides of quadrivalent elements are considerably hydrolysed, stannic chloride at $v=8$ being almost completely decomposed and zirconium chloride being hydrolysed to the extent of 35 per cent. at $v=64$. In other salts examined, the hydrolysis was in the following order: ferric chloride, uranyl chloride, uranyl nitrate, uranyl sulphate, aluminium chloride, aluminium nitrate, aluminium sulphate, beryllium chloride, beryllium nitrate, beryllium sulphate, and the percentage hydrolysis at three dilutions is given. The hydrolysis is not noticeable, or is too small for measurement in solutions of ammonium, potassium, lithium, manganese, cobalt, cerium, erbium, barium, strontium, calcium, and magnesium chlorides, and in silver, manganese and cobalt nitrates. In general, the chlorides appear to be hydrolysed to the greatest extent, then the nitrates, and the sulphates least. The results are in good accord with those of Ley and the temperature coefficient of the hydrolysis may in some cases be estimated from the two sets of determinations.

L. M. J.

Catalysis with Normal Salts. By HANS EULER (*Zeit. physikal. Chem.*, 1900, 32, 348—359).—The inversion of sugar and the catalysis of esters by acids are both accelerated in the presence of normal salts. In the former case, the influence of a small quantity of a normal salt is nearly independent of the sugar concentration, whilst the acceleration due to the normal salt is the more marked the more dilute the acid is. On the supposition that all chemical compounds are electrolytes, and that every catalytic action consists in a change of concentration of the ions involved, the author considers that the accelerating action of normal salts is due to an increased osmotic pressure of the sugar and ester ions, or to an increased reactive capacity on the part of the water. Normal salts may increase the dissociating power of the solvent, and thus increase the osmotic pressure of the sugar and ester, whilst on the other hand the normal salt may increase the number of hydrogen and hydroxyl ions formed from the water.

J. C. P.

Colloidal Solutions. By GEORG BREDIG and A. COEHN (*Zeit. physikal. Chem.*, 1900, 32, 129—132).—Stoeckl and Vanino (this vol., ii, 11) add nothing new regarding colloidal solutions, the evidence recorded having been previously stated by Linder and Picton (*Trans.*, 1892, 61, 137, 148, 1895, 67, 63) and by Barus and Schneider (*Abstr.*, 1891, 1412). Stark's view that precipitation is due to the separation of dissolved air (*Abstr.*, 1899, ii, 644) is untenable, as colloidal solutions under reduced pressure evolve air without precipitation and may afterwards be precipitated by dilute sulphuric acid and other electrolytes.

L. M. J.

Stereoisomerides and Racemic Compounds. By HERMAN C. COOPER (*Amer. Chem. J.*, 1900, 23, 255—261).—The solubility curves for sodium hydrogen dextro- and lævo-tartrates in aqueous solutions of dextrose are coincident. The same holds for the two optically active sodium ammonium tartrates.

In a discussion on partial racemism, the possibility of obtaining a racemic compound the active components of which are not chemically equivalent is suggested.

T. H. P.

Recognition of Racemic Compounds. By GIUSEPPE BRUNI (*Gazzetta*, 1900, 30, i, 35—39).—The method given by Roozeboom (*Abstr.*, 1899, ii, 276 and 401) for the recognition of racemic compounds, pseudoracemic mixtures, and inactive conglomerates by means of their melting point curves has a complete analogue in the author's method, in which the solubility is examined; in place, however, of the ordinary curves of solubility, in which the latter is considered as a function of the temperature, solubility curves are made use of, which only consider the relative quantities of the two enantiomorphous isomerides present and take no account of the solvent. The various types of such solubility curves, which are similar to the melting point curves of Roozeboom (*loc. cit.*), are as follows. For a racemic compound, the curve consists of three distinct parts and has two minima and a maximum, which may, however, be less than or greater than

the solubility of either of the components; for an inactive conglomerate, the curve is composed of two parts with one minimum, whilst the curve corresponding with a pseudoracemic mixture is continuous.

T. H. P.

Water of Crystallisation. II. By THEODOR SALZER (*J. pr. Chem.*, 1900, [ii], 61, 157—165. Compare Abstr., 1895, ii, 488, and 1898, i, 315).—Calcium malonate and methylmalonate are held to be trimolecular, since when air dried they have the composition $\text{CaC}_3\text{H}_2\text{O}_4 + 1\frac{1}{3}\text{H}_2\text{O}$ and $\text{CaC}_4\text{H}_4\text{O}_4 + 1\frac{1}{3}\text{H}_2\text{O}$; the salts $\text{CaC}_3\text{H}_2\text{O}_4 + 4\text{H}_2\text{O}$ and $\text{CaC}_3\text{H}_2\text{O}_4 + 2\text{H}_2\text{O}$ are also found to be less soluble than the anhydrous salt. Calcium propylmalonate has the composition $\text{CaC}_6\text{H}_8\text{O}_4 + 2\text{H}_2\text{O}$; the butylmalonate, $\text{CaC}_7\text{H}_{10}\text{O}_4 + 2\text{H}_2\text{O}$, loses all its water of crystallisation at 110° ; the dimethylmalonate forms readily soluble needles, $\text{CaC}_5\text{H}_6\text{O}_4 + 3\text{H}_2\text{O}$, loses its water of crystallisation at 110° , and begins to decompose at 162° , whilst the acid first melts at 192° ; the methylmalonate crystallises with $3\text{H}_2\text{O}$. The author withdraws his earlier conclusions with regard to the water of crystallisation of calcium malonate and its homologues.

Other examples of salts which are to be regarded as trimolecular are Fittig's barium propylitaconate, $\text{BaC}_8\text{H}_{10}\text{O}_4 + 1\frac{1}{3}\text{H}_2\text{O}$, and calcium dimethylfumarate, which loses two-thirds of its water of crystallisation when heated.

On repeating the work of Rahlis (*Annalen*, 1879, 198, 106), it is found that calcium *o*-bromobenzoate crystallises with only $2\text{H}_2\text{O}$ and is therefore in agreement with Rule VIII (Abstr., 1898, i, 315). Calcium *p*-bromobenzoate, when prepared from calcium chloride and the ammonium salt at the ordinary temperature, crystallises in minute needles containing $3\text{H}_2\text{O}$, in agreement with Rule VIII, but when the solution is evaporated on a water-bath, separates in tablets with $1\text{H}_2\text{O}$.

T. M. L.

Relation of the Taste of Acid Salts to their Degree of Dissociation. By LOUIS KAHLBERG (*J. Physical Chem.*, 1900, 4, 33—37).—Experiments on the taste of acids have indicated that the sour taste is ascribable to the hydrogen ions (Richards, Abstr., 1898, ii, 209). Experiments with acid sodium salts of a number of slightly dissociated acids prove, however, that the sour taste is obtained at concentrations of the hydrogen ion far below the limit for acids which had been previously found, and that the sour taste of these acid sodium salts cannot be ascribed to the hydrogen ions present. It hence appears that it must be due to the acid ion, and owing to the discrepancy between these results and those of Richards, the author considers the explanation of the sour taste from the standpoint of the dissociation theory to be unsatisfactory (see also Höber and Kiesow, Abstr., 1899, ii, 206).

L. M. J.

Laboratory Apparatus for Roasting Large Quantities of Material. By G. PAUL DROSSBACH (*Ber.*, 1900, 33, 486).—The apparatus consists of a horizontal metal tube, open at one end and provided with a gas delivery tube at the other; it carries a hopper on its upper

surface, and is fitted with a worm worked by a grooved wheel and cord. The whole may be heated in a furnace; the worm fits loosely into the tube, so that no lubricant is required. J. J. S.

Inorganic Chemistry.

Volumetric Composition of Hydrogen Fluoride. By HENRI MOISSAN (*Compt. rend.*, 1900, 130, 544—548).—The volumetric composition of hydrogen fluoride was determined (1) by electrolysing aqueous hydrogen fluoride, collecting and measuring the liberated hydrogen, and the oxygen formed by the fluorine acting on the water, and (2) by allowing a measured volume of fluorine to act on water, the liberated oxygen being measured, and the quantity of hydrofluoric acid formed being estimated by titration. In all cases, the ozone in the oxygen was either decomposed by heating or estimated by titration. The results show that hydrogen fluoride is formed by the union of equal volumes of hydrogen and fluorine.

C. H. B.

Vapour Density of Sulphur. By CARL SCHALL (*Ber.*, 1900, 33, 484—485).—A reply to adverse criticisms by Bleier and Cohn (this vol., ii, 203). Further determinations of the vapour density of sulphur at low pressures (to 42·7 mm.) give densities varying from 7·15 to 7·5 compared with oxygen.

J. J. S.

Products of the Action of Sulphur Dioxide on Ammonia. By HANS SCHUMANN (*Zeit. anorg. Chem.*, 1900, 23, 43—66. Compare Divers and Ogawa, *Trans.*, 1900, 77, 327).—The action of dry sulphur dioxide on dry ammonia results in the formation of the compound SO_2NH_3 in the presence of excess of sulphur dioxide, and in the formation of the compound $\text{SO}_2\cdot 2\text{NH}_3$ in the presence of excess of ammonia. The condensation is effected in a flask cooled at 0° , one of the gases being passed through mercury, the other gas entering above the mercury. It is essential that the gases should be carefully dried.

The compound SO_2NH_3 is a yellow, crystalline powder, very hygroscopic, and at once decomposed by water, yielding a faintly acid solution, which, on the addition of acids, evolves sulphur dioxide without the immediate precipitation of sulphur; the freshly prepared solution contains ammonium salts and sulphuric, sulphurous, thiosulphuric, trithionic, and pentathionic acids.

The compound $\text{SO}_2\cdot 2\text{NH}_3$, prepared in a flask cooled at -5 to -7° , forms red fragments, and nodular, seemingly crystalline conglomerates, is not so hygroscopic as the preceding compound, and remains undecomposed for some time on exposure to the air, but gradually changes into a white powder. It dissolves in water, with evolution of ammonia; the solution gives a transitory carmine coloration on the addition of

acids, and when freshly prepared, contains the same acids as that of the preceding compound.

The compound SO_2NH_3 , when heated under dry carbon disulphide in a reflux apparatus, decomposes with evolution of ammonia, and forms a dark red, crystalline sublimate of the composition $3\text{SO}_2\cdot 4\text{NH}_3$, which is very hygroscopic, and yields a solution in water similar to that of the compound $\text{SO}_2\cdot 2\text{NH}_3$.

Potassamide, when heated in sulphur dioxide at 200° , undergoes a violent reaction, with evolution of light and heat; the products are a mixture of the compounds SO_2NH_3 and $\text{SO}_2\cdot 2\text{NH}_3$, and a residue containing potassamide, potassium, sulphur dioxide, and small quantities of ammonia.

Similar compounds are obtained by the action of sulphur dioxide on the anhydrous fatty amines, when brought into direct contact without the presence of a solvent at about -6° . Ethylamine yields the compound $\text{SO}_2\text{NH}_2\text{Et}$, which crystallises in yellow scales and yields a colourless solution in water containing the amine and sulphuric, sulphurous, thiosulphuric, trithionic, and pentathionic acids. The compound SO_2NHMe_2 , obtained from dimethylamine, is a yellow, crystalline mass, and with water gives a faintly acid solution which contains the amine and sulphuric, sulphurous, and thiosulphuric acids only.

E. C. R.

Reduction of Selenium Dioxide by Sodium Thiosulphate. By JAMES F. NORRIS and HENRY FAY (*Amer. Chem. J.*, 1900, 23, 119—125).—The interaction between selenium dioxide and sodium thiosulphate (*Abstr.*, 1897, ii, 70) probably takes place thus: $\text{SeO}_2 + 4\text{Na}_2\text{S}_2\text{O}_3 = 2\text{Na}_2\text{S}_4\text{O}_6 + \text{Se} + 2\text{Na}_2\text{O}$; in concentrated solutions, selenium is precipitated, and the solution becomes alkaline, but in dilute solution no selenium is precipitated, and the reaction is not complete according to this equation, owing to the sodium hydroxide formed neutralising part of the selenious acid, which, therefore, does not enter into reaction. In presence of hydrochloric acid, the action occurs according to the equation: $\text{SeO}_2 + 4\text{Na}_2\text{S}_2\text{O}_3 + 4\text{HCl} = \text{Na}_2\text{S}_4\text{SeO}_6 + \text{Na}_2\text{S}_4\text{O}_6 + 4\text{NaCl} + 2\text{H}_2\text{O}$. No selenium is precipitated, but *sodium selenotetrathionate* is formed, which, although it cannot be isolated, gives Debus's tests for pentathionates (*Trans.*, 1888, 53, 278), with the difference that selenium, not sulphur, is precipitated; a dilute solution of the salt can be boiled without change, but stannous chloride precipitates selenium in a few minutes; sodium thiosulphate effects the same result, but more slowly. The sodium tetrathionate, formed according to the equation, was isolated and identified.

An acid solution of tellurium dioxide yields, with sodium thiosulphate, a solution apparently containing a compound analogous to a selenotetrathionate; this is remarkable, since no compounds of tellurium analogous to the thionates are known.

Incidentally, the authors point out that in presence of dilute acids the starch reaction for iodine is about 0.2 per cent. more sensitive at 3° than at the ordinary temperature.

W. A. D.

Preparation of Pure Tellurium. By JAMES F. NORRIS, HENRY FAY, and D. W. EDGERLY (*Amer. Chem. J.*, 1900, 23, 105—119).—The

basic tellurium nitrate obtained by dissolving tellurium in nitric acid is not hygroscopic, and appears to have the composition $4\text{TeO}_2, \text{N}_2\text{O}_5 + \text{H}_2\text{O}$, rather than $4\text{TeO}_2, \text{N}_2\text{O}_5 + 1\frac{1}{2}\text{H}_2\text{O}$ (Klein and Morel, *Abstr.*, 1884, 1256, and 1885, 16); since water is not given off on heating the salt until about 190° , when decomposition begins, it is probably present combined according to the formula $\text{Te}_2\text{O}_3(\text{OH})(\text{NO}_3)$. The tellurium obtained by dissolving the oxide prepared from the pure nitrate in pure hydrochloric acid, precipitating with sulphur dioxide, and distilling the metal so obtained, on careful examination does not show the presence of any other element.

The double bromide of tellurium and potassium, prepared from tellurium dioxide, hydrobromic acid, and potassium bromide, was fractionally crystallised by a process involving over 200 crystallisations; since the last fractions, when converted into the nitrate, gave practically the same loss of weight on ignition as the earlier ones, no evidence could be obtained by this process in favour of Brauner's view (*Trans.*, 1889, 55, 382; 1895, 67, 549) that tellurium is a mixture of "true tellurium" with an atomic weight of about 125 and another element with a higher atomic weight. The abnormal position of tellurium in the eighth group of the periodic classification of the elements still awaits explanation.

W. A. D.

Specific Gravity and Electrical Resistance of Tellurium. By VICTOR LENHER and J. LIVINGSTON R. MORGAN (*J. Amer. Chem. Soc.*, 1900, 22, 28—31).—The specific gravity of powdered tellurium, obtained by reduction of the alkaline solution of the oxide by sugar, was determined by the pyknometer method. The values obtained varied from 6.194 to 6.204, with a mean of 6.1993. For the determination of the electrical resistance, the molten metal was allowed to solidify in glass tubes of narrow bore jacketed by outer tubes also containing melted tellurium. Great difficulty was found, however, in obtaining uniform results, the values for the specific resistance varying from 279 to 1152; the mean is about 500, but the authors consider that the lower results are probably the more correct. The value obtained by Matthieson was about 2000, so that the structure has an enormous influence on the conductivity. It was observed that the metal expands slightly immediately after solidification, all the tubes cracking at this point, no matter how slowly they were cooled.

L. M. J.

Surface-tensions of Mixtures of Sulphuric Acid and Water, and the Molecular Mass of Sulphuric Acid. By CHARLES E. LINEBARGER (*J. Amer. Chem. Soc.*, 1900, 22, 5—11).—By the aid of the apparatus previously described by the author (*Abstr.*, 1897, ii, 247), measurements were made of the surface tension of aqueous sulphuric acid at concentrations varying from 2.65 to 95 per cent., and at temperatures varying from 0° to 70° . It was found the surface tension of both acid and water is raised by addition of the other component, the composition of the mixture possessing the highest surface tension being about 60 per cent., but varying slightly with temperature. For the higher concentrations, the influence of temperature is very slight, and this should indicate a high degree of polymerisation, so that the molecule of sulphuric acid is probably very complex, and this

complexity may account for many of the extraordinary properties of mixtures of sulphuric acid and water. According to the views of Brühl (Abstr., 1896, ii, 163), it should be a compound of high dissociative power, and the maximum conductivity of solutions of water in sulphuric acid at a concentration of 10 per cent. are probably to be ascribed to the dissociation of the water, the fall with increased concentration being due to the increased viscosity.

L. M. J.

A New Nitrogen Iodide, N_3I . By ARTHUR HANTZSCH (*Ber.*, 1900, 33, 522—527).—On adding an ethereal solution of iodine to silver azoimide suspended in water at 0° , extracting with ether, and allowing the latter to evaporate below 0° , a nearly colourless solid is obtained, which, from a determination of the ratio of nitrogen to iodine in a freshly prepared aqueous solution, appears to have the composition N_3I ; the dry substance often decomposes spontaneously with great violence, giving rise to nitrogen and iodine, whilst the same products are formed when slow decomposition occurs in benzene or chloroform solution. An aqueous solution of the iodide is at first neutral to litmus, and produces no coloration with starch solution, but decomposition occurs somewhat rapidly to azoimide and hypoiodous acid, which is then further resolved into iodine and iodic acid. Aqueous silver nitrate gives rise, similarly, to silver azoimide, iodine, and iodic acid, a reaction which furnishes the means of determining the ratio of iodine to nitrogen present in the compound.

All attempts to prepare the condensation product N_6 were unsuccessful.

W. A. D.

Nitrogen Iodide. By C. HUGOT (*Compt. rend.*, 1900, 130, 505—508. Compare Chattaway, *Trans.*, 1896, 69, 1572; *Proc.*, 1899, 15, 17).—When ammonia gas is passed into a cooled vessel containing iodine, a dark brown liquid is first produced; this becomes red, and finally assumes a faint yellow colour, whilst the compound, $NI_3 \cdot 3NH_3$, separates in dark green needles. The yellow liquid contains the ammonio-ammonium iodide, $NH_4I \cdot 3NH_3$, dissolved in liquid ammonia, together with small quantities of free iodine, and the compound $NI_3 \cdot 3NH_3$. The reaction appears to take the following course: $16NH_3 + 6I = 3(NH_4I \cdot 3NH_3) + NI_3 \cdot 3NH_3$.

The ammonio-nitrogen iodide, $NI_3 \cdot 3NH_3$, when maintained at a temperature of -30° in a vacuum, loses one-third of its ammonia, and a well-defined, crystalline, yellow compound, $NI_3 \cdot 2NH_3$, is produced; at 0° in a vacuum, the latter substance parts with half its ammonia, yielding violet needles of the compound $NI_3 \cdot NH_3$. It is not possible to eliminate the last mol. of ammonia, since the third compound is decomposed on warming, and at about 50° a violent detonation is produced.

G. T. M.

The Molecule of Carbon and the Supposed Negative Heat of Formation of various Carbon Compounds. By WILHELM VAUBEL (*Zeit. angew. Chem.*, 1900, 60—63).—Calculations based on the difference between the heats of combustion of carbon and carbon monoxide lead the author to the conclusion that the molecule of

carbon at its boiling point contains 24 atoms. The heat of dissociation of this complex carbon molecule is taken as 32300 cal., and hence it is deduced that acetylene, carbon disulphide, and other compounds which have commonly negative heats of formation assigned to them, have really positive heats of formation. The author proposes to recalculate on this new basis the heats of formation of organic compounds.

J. C. P.

Preparation of Amorphous Silicon, Silicon Sulphide, Silicon Chloride, and Thiosilicates. By WALTHER HEMPEL and VON HAASY (*Zeit. anorg. Chem.*, 1900, 23, 32—42).—Amorphous silicon is prepared easily and in considerable quantities by heating sodium in an atmosphere of silicon fluoride. The apparatus, which is figured in the original paper, consists of a generator of silicon fluoride and a special iron retort so arranged that when heated and filled with silicon fluoride, sodium can be expeditiously introduced in successive small portions. The product consists of silicon, sodium fluoride, and sodium silicofluoride; it is powdered and heated with sufficient sodium to decompose the silicofluoride and with sufficient aluminium to form an alloy containing not more than 16 per cent. of silicon. When cold, the alloy is separated mechanically from the fused mass, and the aluminium dissolved in hydrochloric acid. The amorphous silicon is lead-grey, amounts to 90—95 per cent. of the theoretical yield, and contains 3—4 per cent. of silica; this is extracted with hydrofluoric acid, and brown, amorphous silicon, amounting to 60—62 per cent. of the theoretical yield, is obtained in a very active form, which, when gently heated in the air, burns to silica. By melting aluminium with silicon, alloys containing up to 22·5 per cent. of silicon can be prepared, but the silicon separated from these is very inert. Silicon from an alloy containing 16·5 per cent. burns in chlorine at 280°, that from an alloy containing 22·5 per cent. at 340—350°.

Silicon sulphide is obtained by melting amorphous silicon with three times its weight of sulphur, and then throwing the fused mass into a red-hot crucible in successive small portions. The product contains 92—95 per cent. of silicon sulphide mixed with silicon and silica, and is purified by sublimation under diminished pressure. It crystallises in beautiful, long, white needles. Silicon chloride is easily prepared by heating the amorphous silicon in a current of chlorine.

Sodium metathiosilicate, Na_2SiS_3 , obtained by melting pure sodium sulphide with silicon sulphide, is a brownish-black mass which evolves hydrogen sulphide when treated with water, yielding a solution which does not evolve more hydrogen sulphide when treated with acids; when treated with chlorine, it yields sulphur chloride and silicon chloride with development of much heat. The authors have applied this last reaction to detect the presence of thiosilicates in some complex silicates, and obtained the following results: ultramarine, 0·174 per cent. SiS_2 ; blast furnace slags, 0·043, 0·009, and 0·104 per cent. SiS_2 ; lava from Vesuvius, 0·007 per cent. SiS_2 . They also point out that the sulphur present in many of the sulphur springs may be due to the decomposition of thiosilicates.

E. C. R.

Preparation of Arsenides, Antimonides, and Alloys of the Alkali Metals. By PAUL LEBEAU (*Compt. rend.*, 1900, 130, 502—505).—Impure arsenides containing excess of the metal or arsenic are produced when the latter or its hydride, either in the gaseous or liquid state, reacts with an alkali metal. Liquefied hydrogen arsenide has no solvent action on the alkali metals, and, unlike liquid ammonia, does not form compounds with these elements.

Pure sodium arsenide, Na_3As , is prepared by heating to redness in a closed iron vessel a mixture of arsenic and sodium; an excess of the latter is employed and the uncombined metal is removed from the cooled product by means of liquid ammonia; the arsenide remains undissolved and is obtained in the form of small, black crystals. Sodium antimonide, bismuthide, and stannide, and the corresponding lithium and potassium compounds, have been produced in a similar manner.

G. T. M.

Electrolytic Formation of Potassium Chlorate. By ANDRÉ BROCHET (*Compt. rend.*, 1900, 130, 718—721. Compare this vol., ii, 205).—When a cold and almost neutral solution of potassium chloride is electrolysed, the whole of the electric energy is spent in producing hypochlorite; the greater portion of this substance, however, is at once transformed into chlorate, the transformation being accompanied by an evolution of oxygen; under certain conditions, the addition of potassium chromate prevents the decomposition of the hypochlorite. This transformation is made manifest on electrolysing a solution of potassium chloride containing potassium dichromate; this salt liberates hypochlorous acid, becoming itself converted into the neutral chromate, and the colour of the solution changes from orange to yellow; the change is reversed when the solution is left for twelve hours owing to the production of chloric acid, this acid partially displacing chromic acid and regenerating the dichromate.

The auto-oxidation of hypochlorous acid takes place even more rapidly in hot or alkaline solutions, the yield of available chlorine being correspondingly diminished.

G. T. M.

Presence of Potassium Nitrite in Brown Powder Residue when the Powder is Burnt in Air under Ordinary Pressure. By A. M. SETON and K. L. STEVENSON (*Chem. News*, 1899, 80, 221).—Brown powder burns more slowly than black powder, and leaves more residue, which is generally white or greyish-white, hygroscopic, and partly soluble in water. A complete analysis gave the following results: K_2CO_3 , 61.96; K_2SO_4 , 26.18; KNO_2 , 6.17; insoluble, 5.8 per cent.

D. A. L.

Isomeric Potassium Sodium Sulphites. By GEORGE S. FRAPS (*Amer. Chem. J.*, 1900, 23, 202—214).—The existence of two isomeric potassium sodium sulphites has been indicated by the work of Röhrig (Abstr., 1888, 649), Schwicker (Abstr., 1889, 942), and Barth (Abstr., 1892, 564). The author prepares the double sulphite, firstly, by dissolving sodium carbonate in a solution of potassium hydrogen sulphite, and, secondly, by the interaction of potassium carbonate and sodium hydrogen sulphite; from a number of experiments on the action of

ethyl iodide on these two products, it is concluded that there is no evidence of the existence of two isomeric double sulphites.

T. H. P.

Compounds of Metals among themselves. By NICOLAI S. KURNAKOFF (*J. Russ. Phys. Chem. Soc.*, 1899, 31, 927—948).—The relations between melting point and composition are given for the following mixtures: mercury and sodium, mercury and potassium, cadmium and sodium, lead and sodium, bismuth and sodium.

The melting point curve for sodium and mercury shows five transition points, at which the ratio of the number of atoms of sodium to the number of mercury atoms has the values: 5·690 : 1 (at 21·25°); 2·559 : 1 (at 67·0°); 1·020 : 1 (at 209·7°); 1 : 1·101 (at 218°); 1 : 4·571 (at 155°). The maximum melting point corresponds with the compound NaHg_2 . From the eutectic mixture ($\text{Na} : \text{Hg} = 5·690 : 1$), beautiful, hexagonal plates of indefinite composition separate. The compound Na_3Hg , described by Maey (Abstr., 1899, ii, 547), has probably the composition Na_nHg , where n is not greater than 2·559. For potassium-mercury, the curve has three transition points, namely, 195·0°, 129·0°, and 70·3°, the corresponding values for the ratio $\text{K} : \text{Hg}$ being 1 : 3·283, 1 : 6·350, and 1 : 10·556 respectively. The maximum melting point mixture has the composition KHg_2 . The compound KHg_{12} , described by several writers, is probably KHg_n , n being not greater than 10·556; Maey (*loc. cit.*) found that n does not exceed 11. From the researches of the author and others, definite compounds of sodium and mercury of the composition NaHg_n are shown to exist, as follows: (1) n less than 2·5 (NaHg_2); (2) NaHg ; (3) n between 1 and 2; (4) NaHg_2 ; (5) n between 2 and 5 (NaHg_3); (6) NaHg_5 or NaHg_6 . The definite mercury potassium compounds, having the formula KHg_n , are: (1) KHg ; (2) KHg_2 ; (3) n between 2 and 3·28 (KHg_3); (4) n between 3·28 and 6·3 (KHg_5 or KHg_6); (5) n between 6·3 and 10·5 (KHg_{10}).

The maximum points of the other curves correspond with compounds having the formulæ NaCd_2 , NaPb , and Na_3Bi . NaCd_2 separates in glistening octahedra.

T. H. P.

Persulphates of Rubidium, Cæsium, and Thallium. By HUGH MARSHALL (*J. Amer. Chem. Soc.*, 1900, 22, 48. Compare Abstr., 1899, ii, 747).—Rubidium and cæsium persulphates, obtained by double decomposition from ammonium persulphate, are isomorphous with the ammonium salt, whereas mixtures of these salts with the potassium salt crystallise in monoclinic crystals. Mixtures of the thallos and ammonium salts also crystallise in the monoclinic system, and are isomorphous with the preceding mixtures.

J. J. S.

Melting Point of Lithium. By GEORG W. A. KAHLBAUM (*Zeit. anorg. Chem.*, 1900, 23, 220—221).—The sample of lithium was prepared by A. Guntz by the electrolysis of a mixture of equal parts of lithium and potassium chlorides. The melting point was determined in a bath of dry paraffin, and found to be 186° (Bunsen and Matthiessen give 180°).

E. C. R.

Action of Hydrogen Peroxide on Barium Hydroxide. By ROBERT DE FORCRAND (*Compt. rend.*, 1900, 130, 716—718).—When

baryta water containing 1 mol. of barium hydroxide is treated with $\frac{1}{2}$ mol. of hydrogen peroxide, a precipitate is formed in 3 minutes, even in dilute solutions; the heat evolved during the first 2 minutes is 3.121 Cal., and this represents the heat of the reaction before the formation of any insoluble compound; when twice this quantity of the peroxide is employed, the heat generated is somewhat greater, namely, 4.350 Cal., and the immediate addition of 2 mols. of hydrochloric acid produces a further thermal change of 23.474 Cal. The addition of 2 and 3 mols. of the peroxide to two solutions, each containing 1 mol. of the barium compound, is accompanied by the development of 7.801 and 8.552 Cal. respectively, the corresponding heats of neutralisation by hydrochloric acid (2 mols.) being 19.958 and 18.984 Cal. The heat developed on adding 10 mols. of the peroxide to the solution of barium hydroxide is 12.261 Cal., and the heat of neutralisation by hydrochloric acid is 15.345 Cal.; when a larger excess of the peroxide (30 mols.) is employed, the thermal effect is 13.586 Cal. Two compounds appear to be successively produced, one, containing a large proportion of hydrogen peroxide, which has not been isolated, the other being the substance $\text{BaO}_2 \cdot \text{H}_2\text{O}_2$ studied by Schoene and Berthelot; the latter may be regarded as having the constitution $\text{Ba}(\text{O} \cdot \text{OH})_2$. The heat of neutralisation of this compound by barium hydroxide is 0.899 Cal., or 0.45 Cal. for each hydroxyl group; it appears, therefore, that the compound is slightly acidic. The formula $\text{Ba} \begin{smallmatrix} \text{O} \cdot \text{O} \\ \diagup \quad \diagdown \\ \text{O} \cdot \text{O} \end{smallmatrix} \text{Ba}$ is ascribed to the salt produced.

G. T. M.

Action of Metallic Magnesium on Water. By EDWARD G. BRYANT (*Chem. News*, 1899, 80, 211—212).—Magnesium of commerce, containing 1.77 per cent. of iron and 0.3 of calcium, but no detectable carbon, was found to evolve hydrogen when placed in water, the action continuing for many hours with decreasing energy, and finally ceasing. 0.1 gram of the powdered metal, placed in 100 c.c. of water, yielded 2—3 c.c. of hydrogen; this quantity could be increased by the addition of normal sodium sulphate, which dissolves magnesium oxide; heating the water did not cause a greater, but only a more rapid, evolution of hydrogen. The metal itself became tarnished, and, if polished, regained its activity. There was no question of a couple forming, and the gases in water were shown to have no effect on the action, which is a direct action of magnesium on water. One part of magnesium oxide dissolves in 225,000 parts of water. D. A. L.

Colloidal Cadmium. By GEORG BREDIG (*Zeit. physikal. Chem.*, 1900, 32, 127—8. Compare this vol., ii, 213).—Colloidal metallic solutions have been proved to consist of minute suspended particles of metals, and it hence follows that colloidal solutions of metals with a lower potential than hydrogen, such as cadmium or zinc, would be unstable and difficult to obtain. By means of an E.M.F. of 30—40 volts and a current of 5—10 amperes, an arc may be obtained between cadmium electrodes immersed in pure, air-free water, the cadmium being dispersed with the formation of a deep brown colloidal solution which changes to a blue-green, and coagulates on the addition of

electrolytes. By exposure to air, the solution speedily oxidises, but by exclusion of air, especially if the liquid be thickened by gelatin, it may be kept for a considerable time. L. M. J.

Action of Hydrogen Sulphide on Lead Peroxide. By LUDWIG VANINO and OTTO HAUSER (*Ber.*, 1900, 33, 625).—When hydrogen sulphide is passed over either moist or dry lead peroxide, the whole mass glows, and the gas burns with the characteristic lead flame. The reaction can be used, not merely as a lecture experiment, but may also be employed for starting an explosion, even with guncotton saturated with moisture. The reaction works best when the peroxide is collected in small heaps and not spread over a flat surface. Bismuth and silver peroxides give the same reaction, but lead oxide, manganese peroxide, cobaltic hydroxide, or cupric oxide do not. J. J. S.

A New Type of Ammonio-copper Chromate. By M. C. SCHUYTEN (*Chem. Centr.*, 1900, i, 399—400; from *Bull. Acad. roy. Belg.*, [iii], 37, 649—656).—By treating an aqueous solution of copper sulphate and potassium dichromate with ammonia, or by adding potassium dichromate to an ammoniacal solution of cupric hydroxide from which the excess of ammonia has been removed by exposure to the air, a compound, $4\text{CuCrO}_4 \cdot 3\text{NH}_3 \cdot 5\text{H}_2\text{O}$, separates as a brown, amorphous powder; when heated, it evolves ammonia, water, and a small quantity of nitrous fumes, but the whole of the ammonia and water cannot be expelled even by heating for a long time at a high temperature. It dissolves in hydrochloric acid or ammonia, forming a yellow or a green solution respectively; it is also easily soluble in a solution of silver nitrate, but insoluble in organic solvents. Alcohol is not oxidised to aldehyde by boiling with the hydrochloric acid solution of this compound. E. W. W.

Mercury Derivatives of Nitrogen Compounds. By KARL A. HOFMANN and EDUARD C. MARBURG (*Zeit. anorg. Chem.*, 1900, 23, 126—134. Compare *Abstr.*, 1899, i, 486).—In answer to Pesci's criticisms (*Abstr.*, 1899, ii, 750), the authors maintain the correctness of their formulæ for the fusible and infusible precipitates obtained from mercuric chloride and ammonia in the presence of ammonium chloride. They point out that these compounds, HgNH_2Cl and $\text{Hg}(\text{NH}_3)_2\text{Cl}_2$, correspond with the ethylamine derivatives, HgNHEtCl , HgNH_2EtCl , and $\text{Hg}(\text{NH}_2\text{Et})_2\text{Cl}_2$, whereas ethylamine derivatives corresponding with compounds of the formulæ Hg_2NCl , NH_4Cl and $\text{Hg}_2\text{NCl} \cdot 3\text{NH}_4\text{Cl}$, could not be formed from an ethylated ammonia. The decomposition of the fusible and infusible precipitates by dilute alkalis naturally results in the formation of the theoretical quantity of mercuriammonium chloride, the first products of decomposition being alkali chloride, mercuric oxide and oxychloride, and ammonia; the mercuric oxide and ammonia, in the presence of halogen, then form the chloride of Millon's base and from 2 mercury atoms 1 mol. of mercuriammonium chloride is formed, 1 mol. of ammonia retained, and the excess of ammonia evolved.

Pesci's formulæ for Millon's base, $\text{Hg}_2\text{N} \cdot \text{OH} \cdot 2\text{H}_2\text{O}$, and the mercuriammonium salts, Hg_2NX , do not explain the behaviour of these

compounds on dehydration. Millon's base becomes dark brown on dehydration and the resulting compound, Hg_2NOH , is explosive and does not combine with hydrogen chloride to form salts. The salts of Millon's base are represented by the formula $(\text{HgOH})_2\text{NH}_2\text{X}$ and cannot be dehydrated without decomposition. The only exception is the nitrate, HgN, NO_3 , which, when prepared from Millon's base, is not pure and on heating yields a small quantity of water. E. C. R.

Anhydrous Dimercuriammonium Iodide, Amorphous and Crystalline. By MAURICE FRANÇOIS (*Compt. rend.*, 1900, 130, 571—573).—Dimercuriammonium iodide, contrary to the usual statements, contains neither hydrogen nor oxygen, but is anhydrous and is a very stable substance. It is obtained in an amorphous state by the action of a large excess of concentrated ammonia solution on mercuric iodide or mercuridiammonium iodide, or, better, by the prolonged and repeated action of a 25 per cent. solution of sodium hydroxide on mercuridiammonium iodide. The crystallised compound is prepared by mixing a saturated solution of mercuridiammonium iodide in concentrated ammonia solution with twice its volume of the same concentrated ammonia solution. The crystals form slowly and are very dark purple by reflected light, but dark red brown by transmitted light. C. H. B.

Preparation and Properties of a Manganese Perfluoride. By HENRI MOISSAN (*Compt. rend.*, 1900, 130, 622—627).—Metallic manganese is attacked by fluorine at the ordinary temperature, but the reaction is limited by the formation of a layer of fluoride on the surface of the metal. If the manganese is finely powdered, the reaction takes place with incandescence, but the fluoride formed is partly volatilised and decomposed, so that the product is not of constant composition. Manganous fluoride is also attacked by fluorine, but the reaction is never complete, whilst with manganous chloride it is difficult to expel the whole of the chlorine. With manganous iodide, however, the reaction is much more regular, and manganese trifluoride, Mn_2F_6 , is obtained in crystals which preserve the form of those of the iodide from which it was derived, and have a sp. gr. 3.54. When heated, it decomposes with the production of manganous fluoride and fluorine, whilst it is reduced by hydrogen below a red heat, hydrogen fluoride and manganous fluoride being formed. At the ordinary temperature, chlorine, bromine, and iodine are without action on manganese trifluoride, but on heating, ternary compounds are formed, that with iodine being of a red colour. When the trifluoride is heated in glass, the latter is violently attacked, silicon fluoride being liberated, whilst a mixture of fluoride and oxyfluoride of manganese remains. Manganese trifluoride is decomposed by oxygen at a red heat with the formation of black, crystalline oxide of manganese. With sulphur at its boiling point, sulphur fluoride and manganous fluoride are formed; with phosphorus at a slightly elevated temperature, phosphorus trifluoride and pentafluoride are produced; and with arsenic, the trifluoride is obtained. Silicon, boron, and carbon are converted into fluorides by the action of manganese trifluoride. When heated in an atmosphere of hydrogen chloride, manganous

chloride, hydrogen fluoride, and free chlorine are formed. Sulphuric, nitric, and hydrochloric acids dissolve manganese trifluoride, forming dark brown solutions which are decomposed by excess of water. The action of water alone results in the formation of manganous fluoride, hydrofluoric acid, and a hydrated oxide of manganese, the relative proportions of these products depending on the amount of water employed. Manganese trifluoride readily reacts with hydrogen sulphide, sulphur chloride, and sulphuryl chloride, whilst with phosphorus trichloride it yields phosphorus fluorochloride, PF_3Cl_2 , and with phosphorus pentachloride the pentafluoride. With carbon tetrachloride, the products obtained are a white manganese fluoride, chlorine, and carbon fluoride. Organic substances, such as benzene, turpentine, chloroform, alcohol, and ether are without action on manganese trifluoride, even at 100° .

N. L.

Ferric Oxide Solution obtained by Dialysis. By WILLY WOBBE (*Chem. Centr.*, 1900, i, 165; from *Pharm. Centr.-H.*, 40, 793—796).—A solution of ferric oxide may be obtained by dialysing a solution of ferric oxychloride prepared by adding ammonia to a solution of ferric chloride in small portions at a time, so that after each addition the ferric hydroxide is completely dissolved on stirring. The clear, dark brown solution so obtained scarcely tastes of iron. It is evaporated until it contains 3.5 per cent. of iron, and has a sp. gr. 1.05. The last traces of chlorine cannot be removed by dialysis, and the product still contains 0.75 per cent. of ferric chloride, but it is free from ammonium salts. Attempts to completely remove the chloride by a process of hot dialysis appear to promise success. The solutions of ferric oxychloride and of ferric oxide may be boiled for some time without decomposing. The possibility of concentrating a solution of ferric oxychloride by heat renders unnecessary the pressing of the ferric hydroxide in the preparation of the solution for pharmaceutical purposes. After removing the supernatant liquid, the precipitate is added in small portions to the hydrochloric acid, and the solution then evaporated to the required density. E. W. W.

Preparation of the Phosphides of Iron, Nickel, Cobalt, and Chromium. By GEORGES MARONNEAU (*Compt. rend.*, 1900, 130, 656—658).—A number of metallic phosphides were obtained in a well crystallised state by heating a mixture of the finely divided metal with copper phosphide in the electric furnace, the product of the reaction being treated with nitric acid to remove the copper. Iron phosphide, Fe_2P , was thus obtained in the form of whitish-grey, brilliant needles having a sp. gr. 6.57. Nickel phosphide, Ni_2P , crystallises in transparent, grey needles of sp. gr. 6.3, whilst cobalt phosphide, Co_2P , of similar appearance, has a sp. gr. 6.4. Chromium phosphide, CrP , forms dull grey crystals of a sp. gr. 5.71. The phosphides of iron, nickel, and chromium are insoluble in all acids except a mixture of nitric and hydrofluoric acids; cobalt phosphide is dissolved by concentrated nitric acid, and is slowly attacked by hydrochloric and sulphuric acids. N. L.

Alloys of Platinum and Palladium with Cadmium, Zinc, and Magnesium. By W. R. EATON HODGKINSON, R. WARING, and A. P. H. DESBOROUGH (*Chem. News*, 1899, 80, 185).—A weighed quantity of platinum or palladium foil contained in a porcelain boat was placed close to a porcelain boat containing a large excess of the volatile metal and heated above the boiling point of the latter in refractory glass tubing; during the experiment, either a current of dry hydrogen was passed over the volatile metal towards the platinum or a vacuum was induced by means of a Sprengel pump at the platinum end of the tube. At the close of the experiment, the platinum or palladium in the boat was weighed and examined. With platinum, cadmium formed an alloy, PtCd_2 , which was white, crystalline, and brittle, and from which cadmium does not volatilise at full redness; when treated with nitric acid, some platinum dissolved as well as the cadmium. With zinc, the results were less definite, but if heated to a point where the glass tube collapsed, a brittle, crystalline alloy was obtained similar in character to the cadmium alloy, but of the composition PtZn . Magnesium proved still more troublesome, as its vapour was absorbed by the glass, but by lining the tube with magnesium oxide, a friable, crystalline alloy was produced of the composition PtMg_2 .

Experiments with palladium and with nickel have yielded only negative results. D. A. L.

Complex Palladium Salts. By ARTHUR ROSENHEIM and HERRMANN ITZIG (*Zeit. anorg. Chem.*, 1900, 23, 28—31).—*Potassium palladous idonitrite*, $\text{K}_2\text{PdI}_2(\text{NO}_2)_2 + 3\text{H}_2\text{O}$, obtained by saturating a concentrated solution of potassium nitrite with palladous iodide and allowing the mixture to crystallise over sulphuric acid, crystallises in purplish-red, prismatic needles, effloresces on exposure to the air, and decomposes when dissolved in water or treated with dilute acids, with precipitation of palladous iodide.

Potassium pallodous oxalonitrite, $\text{K}_2\text{Pd}(\text{NO}_2)_2\text{C}_2\text{O}_4$, obtained by warming the preceding salt with a molecular proportion of oxalic acid, crystallises in beautiful, yellow needles sparingly soluble in cold, but easily so in hot, water.

Ammonium palladous trichlorosulphite, $(\text{NH}_4)_3\text{PdCl}_3\text{SO}_3 + \text{H}_2\text{O}$, obtained by saturating a concentrated solution of ammonium sulphite with ammonium palladochloride, crystallises in bright red, hexagonal crystals [$a : c = 1 : 0.8923$]. E. C. R.

Mineralogical Chemistry.

Roumanian Petroleum^s. By ALFONS O. SALIGNY (*Chem. Centr.*, 1900, 60; from *Bul. Roumanie*, 8, 351—365).—In the original paper, the physical and chemical properties of 12 kinds of Roumanian

petroleum are described and tabulated. The flash points of the various fractions are given, and their suitability for use as burning oils is also discussed. These petroleum contain very variable amounts of volatile oils, and ethylisobutane and isopropane were found in the fractions boiling below 70°. E. W. W.

Melonite from South Australia. By ALFRED J. HIGGIN (*Trans. Roy. Soc. South Australia*, 1899, 23, 211—212).—This mineral, previously only known from California, has now been found with quartz and calcite at Worturpa, South Australia. The thin lamellæ have a brilliant metallic lustre; the cleavage planes are silver-white to reddish-brown. $H=1.5$; sp. gr., 7.6. Analyses I and II agree with the formula Ni_2Te_3 (compare this vol., ii, 22).

	Te.	Ni.	Au.	Insol.	Total.
I.	74.49	22.99	0.329	2.091	99.90
II.	71.500	21.274	0.018	7.319	100.11

Traces of bismuth and lead are present. On dissolving the mineral in nitric acid, the gold is left as bright spangles. L. J. S.

Titaniferous Magnetites. By JAMES F. KEMP (*School of Mines Quart.*, 1899, 20, 323—356; 21, 56—65).—Titaniferous magnetites, with the exception of the occurrences in sands, are almost invariably found associated with rocks of the gabbro type, and have originated by a process of segregation from the magma. The mineral, as a rule, contains vanadium, chromium, nickel and cobalt, which together may amount to several per cent. (compare *Abstr.*, 1899, ii, 109). Phosphorus and sulphur are low, or entirely absent. A description is given of the occurrence of titaniferous magnetites in each country of the world. Numerous references and analyses are quoted. Although abundant in certain regions, the mineral is not at present worked as an ore. L. J. S.

Manganese Nodules from New South Wales. By WILLIAM M. DOHERTY (*Rept. Australian Assoc. Adv. Sci.*, 1898, 7, 339).—In the scrub-land near Onybygambah, on the Tweed river, are scattered about numerous spherical nodules which are dark and shining, with the appearance of seeds, or dull black; they are soft, and of the size of a pea to that of a Barcelona nut. Analyses gave:

MnO ₂	Fe ₂ O ₃ , Al ₂ O ₃	MgCO ₃	Organic Matter.	Gangue.
24.70	11.20	2.00	12.00	49.60
25.00	8.70	2.60	12.80	50.20
40.60	14.00	3.10	10.00	32.10

L. J. S.

Egyptian Soda Valleys. By G. SCHWEINFURTH and L. LEWIN (*Jahrb. Min.*, 1900, i, 236—237; from *Zeit. Ges. Erdkunde*, 1898, 33, 1—25).—The following analyses of the natural soda, as exported, are given. I. Dirty white nodular concretions. II and III. "Natrûn Sultani," which separates out on the floor of the lakes. IV. Hopper-shaped crystals of salt on the surface of the lakes.

	I.	II.	III.	IV.	V.
$\text{Na}_2\text{CO}_3 + \text{NaHCO}_3 \dots$	85.86	80.56	87.98	0.212	66.80
$\text{NaCl} \dots \dots \dots$	7.00	10.40	4.00	98.00	18.44
$\text{Na}_2\text{SO}_4 \dots \dots \dots$	1.20	3.72	0.59	0.506	11.40

Analysis V is of material found in a tomb near Thebes, dating from 1500—1600 B.C. The lakes are probably supplied by Nile water, and it is suggested that the soda is formed by the interaction of calcium hydrogen carbonate and sodium sulphate, the latter being derived by the interaction of sodium chloride and gypsum. L. J. S.

Formation of Oceanic Salt Deposits, particularly of the Stassfurt Beds. XV. Formation of Glauberite at 25°. By JACOBUS H. VAN'T HOFF and D. CHIARAVIGLIO (*Chem. Centr.*, 1900, i, 59—60; from *Sitzungsber. Akad. Wiss. Berlin*, 1899, 810—818. Compare this vol., ii, 76).—At Leopoldshall, glauberite is found in isolated masses in the older rock salt 30 metres below the potassium chloride stratum, and under the kieserite region. The mineral also occurs in the upper layers of the kainite zone, and single crystals are found in the lower portions of the kieserite bed. When a solution of calcium chloride is mixed with a solution of sodium sulphate, and the mixture stirred and evaporated at 100°, the separation of gypsum is followed by the formation of needles of the compound, $\text{Na}_2\text{Ca}(\text{SO}_4)_2 + 2\text{H}_2\text{O}$, which are then, however, rapidly replaced by rhombohedra of glauberite, the latter change being complete when the liquid has been concentrated. The mother liquor was removed by means of alcohol. Calculations from experimental data and graphical representation of results show that glauberite is formed, together with the following minerals, at 25°: rock salt, epsomite, $\text{MgSO}_4 + 7\text{H}_2\text{O}$; picromerite, $\text{MgK}_2(\text{SO}_4)_2 + 6\text{H}_2\text{O}$; blödite, $\text{MgK}_2(\text{SO}_4)_2 + 4\text{H}_2\text{O}$; thenardite, Na_2SO_4 ; and aphthitalite, $\text{K}_3\text{Na}(\text{SO}_4)_2$, and also that glauberite is not formed when sea water is evaporated at 25°. When crystals of glauberite are left in contact with sea water which is beginning to deposit sodium chloride or magnesium sulphate at 25°, they gradually disappear and gypsum is formed. E. W. W.

Formation of Oceanic Salt Deposits, particularly of the Stassfurt Beds. XVI. Hydrate of Magnesium Potassium Sulphate, $\text{Mg}_4\text{K}_2(\text{SO}_4)_5 + 5\text{H}_2\text{O}$. By JACOBUS H. VAN'T HOFF and N. KASSATKIN (*Chem. Centr.*, 1900, i, 368; from *Sitzungsber. Akad. Wiss. Berlin*, 52, 951—953).—In order to ascertain the conditions of the formation of langbeinite, $\text{Mg}_2\text{K}_2(\text{SO}_4)_3$, obtained by removing water from a mixture of magnesium and potassium sulphates, the progress of dehydration of a system, $\text{MgSO}_4 \cdot 6\text{H}_2\text{O} + \text{MgK}_2(\text{SO}_4)_2 \cdot 4\text{H}_2\text{O}$, prepared by concentrating at 47.2° was followed. A hydrate of magnesium potassium sulphate, $\text{Mg}_4\text{K}_2(\text{SO}_4)_5 + 5\text{H}_2\text{O}$, was formed; it is a double salt of the hydrate, $\text{MgSO}_4 + \frac{5}{4}\text{H}_2\text{O}$ (*Abstr.*, 1899, ii, 759). It is also formed when a mixture of hexahydrated magnesium sulphate and leonite are heated at 72.5°. Its formation is easily recognised by means of the dilatometer or the thermometer, and depends on the mutual action of the salts, for solutions of these salts, when heated alone, do not show any such change. When a solution containing

magnesium sulphate (4 mols.) and potassium sulphate (1 mol.) is evaporated, leonite first separates, then the new compound in well formed needles, and finally the leonite disappears and the whole mass solidifies.

E. W. W.

Formation of Oceanic Salt Deposits, particularly of the Stassfurt Beds. XVII. A Relationship between the Composition of Solutions of Sodium Chloride and Potassium Chloride saturated at 25°. By HAROLD A. WILSON (*Chem. Centr.*, 1900, i, 368—369; from *Sitzungsber. Akad. Wiss. Berlin*, 52, 954—955).—In the diagram representing the relations of solubilities in the case of saturation with potassium chloride in presence of chlorides and sulphates of magnesium and potassium (*Sitzungsber. Akad. Wiss. Berlin*, 1898, 820), it is seen that, in the plane which indicates saturation with sodium chloride and potassium chloride, the data have a very simple relationship. If the composition is expressed in molecules of Na_2Cl_2 (a), K_2Cl_2 (b), MgCl_2 (c) and MgSO_4 (d) per 1000 molecules of water, then $b + c/5$ is a constant, that is, by the entry of each double molecule of potassium chloride, 1/5th of a molecule of magnesium chloride is expelled.

The following data are quoted :

	Saturation with		
	K_2Cl_2	MgCl_2	$\text{K}_2\text{Cl}_2 + \frac{\text{MgCl}_2}{5}$
NaCl and KCl.....	19·5	0	19·5
NaCl, KCl and aphthitalite	20	0	20
NaCl, KCl and carnallite	5·5	70·5	19·6
„ „ glaserite and picromerite.....	16	18·5	19·7
„ „ picromerite and leonite	14·5	25·5	19·6
„ „ leonite and $\text{MgSO}_4 + 6\text{H}_2\text{O}$	13	30·5	19·1
„ „ $\text{MgSO}_4 + 6\text{H}_2\text{O}$ and $\text{MgSO}_4 + 5\text{H}_2\text{O}$	6·5	63	19·1
„ „ $\text{MgSO}_4 + 5\text{H}_2\text{O}$ and carnallite.....	6	68	19·6
„ „ and $\text{MgSO}_4 + 6\text{H}_2\text{O}$	7·8	55·8	19
„ „ picromerite and $\text{MgSO}_4 + 6\text{H}_2\text{O}$...	9·5	42·5	18
„ „ in 20 per cent. MgCl_2	9·5	47·5	19

E. W. W.

Constitution and Classification of Silicates. By VASILE C. BUTUREANU (*Jahrb. Min.*, 1900, i, Ref. 184—186; from *Bul. Soc. Sci. Fis. Bucuresci*, 1896, 60—73, 129—139, 254—279).—The following is the classification given :

I. Neutral silicates.

a. Orthosilicates. General formula, $(\text{SiO}_4)_n(\text{M}'_4)_n$.

(1). Simple.

(2). Condensed.

b. Metasilicates. General formula, $(\text{SiO}_3)_n(\text{M}'_2)_n$.

(1). Simple.

(2). Condensed.

c. Polysilicates. Derived from meta- or ortho-silicic acid : general formulæ $\text{Si}_n\text{O}_{3n+1}\text{M}'_{2n+2}$, $\text{Si}_n\text{O}_{3n}\text{M}'_{2n}$, $\text{Si}_n\text{O}_{3n-1}\text{M}'_{2n-2}$, &c.

II. Basic silicates.

III. Acid silicates.

IV. Silicates with water of crystallisation.

V. Mixed silicates; for example, borosilicates, titanosilicates, &c.

Structural formulæ for each mineral species are given in the original.

L. J. S.

Augite from Yoneyama, Japan. By C. IWASAKI (*Zeit. Kryst. Min.*, 1900, 32, 302; from ? [separate copy, 5 pp.]).—Augite crystals, up to 1 cm. across, occur in a weathered olivine-augite-andesite at Yoneyama, Prov. Echigo. A short, crystallographic description is given; sp. gr. 3.42. Analysis by Yoshida gave:

SiO ₂ .	Fe ₂ O ₃ .	Al ₂ O ₃ .	FeO.	CaO.	MgO.	K ₂ O.	Na ₂ O.	Total.
53.56	2.75	0.26	8.69	30.16	1.70	0.21	2.64	99.97.

L. J. S.

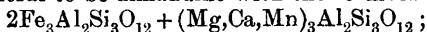
Westanite, Pyrophyllite and Kaolinite from Westana, Sweden. By MATS WEIBULL (*Jahrb. Min.*, 1900, i, Ref., 197—198; from *Geol. För. Förh.*, 1898, 20, 57—66).—A microscopical examination of Blomstrand's westanite shows it to consist of pyrophyllite derived by the alteration of andalusite. Pyrophyllite also occurs at Westana as colourless to yellow, six-sided crystals embedded in kaolinite. The optical properties of these crystals are given; sp. gr. 2.768. At about 600°, the material loses 5.11 per cent. of water, and none is lost below this temperature. The alteration of andalusite to pyrophyllite is expressed by the equation, $(\text{AlO})_2\text{SiO}_3 + 3\text{H}_2\text{SiO}_3 = 2(\text{AlH})(\text{SiO}_3)_2 + 2\text{H}_2\text{O}$.

The granular kaolinite, in which the pyrophyllite is embedded, gave the following results on analysis, agreeing with the usual formula $\text{H}_4\text{Al}_2\text{Si}_2\text{O}_9$,

SiO ₂ .	Al ₂ O ₃ .	MgO.	K ₂ O, Na ₂ O.	H ₂ O.	Total.	Sp. gr.
45.41	40.59	0.07	traces	13.90	99.97	2.598

L. J. S.

[Minerals in] the Pegmatites of the Upper Veltlin. By GOTTLÖB ED. LINCK (*Jenaische Zeit. Naturwiss.*, 1899, 33, 345—360).—The crystalline schists between Sondalo and Bormio are penetrated by pegmatite masses containing quartz, plagioclase, muscovite, biotite and garnet with apatite, tourmaline, dumortierite, chrysoberyl, prehnite, zoisite, epidote and chlorite; descriptions are given of each of these minerals, and analyses of the following. Plagioclase is white and cloudy: I, from Val Lenasco, corresponds with $\text{Ab}_{31}\text{An}_5$; II, from Val Donbastone, with $\text{Ab}_{13}\text{An}_3$; optical determinations are also given. Garnet occurs as light coffee-brown crystals of the form $n\{211\}$; analysis by W. Schimpff of material from Val Donbastone gave III, showing the mineral to be almandine with the formula



the slight excess of silica and alumina is due to alteration. Dumortierite occurs at Val Donbastone as columnar crystals 5 cm. in length; it is pistachio-green or rarely bluish-green, and resembles epidote in appearance. The prism angle is $110^\circ 54'$, and there is a prismatic

cleavage. $H=7$. It is strongly pleochroic; optical determinations are given. Analysis by W. Schimpff gave IV; boron is also present.

	SiO ₂	Al ₂ O ₃	FeO	MnO	CaO	MgO	Na ₂ O	Loss on ignition	Total	Sp. gr.
I.	65·39	21·36	—	—	2·64	—	[10·61]	—	100	2·616—2·617
II.	64·12	22·48	—	—	4·23	—	[9·17]	—	100	2·623—2·625
III.	36·98	24·58	29·68	1·14	0·35	7·78	—	—	100·51	4·010
IV.	36·81	57·27	—	—	1·66	1·38	—	1·31	98·45	3·22

L. J. S.

Ransätite. By MATS WEIBULL (*Jahrb. Min.*, 1900, i, Ref., 187; from *Geol. För. Förh.*, 1898, 20, 53).—A re-examination of the supposed new mineral ransätite (Abstr., 1897, ii, 268) shows it to be an impure manganese garnet enclosing quartz, pyrophyllite, chloritoid, kyanite and ore particles (hæmatite?).

L. J. S.

Tourmaline from Elba. By E. MANASSE (*Jahrb. Min.*, 1900, i, Ref., 192; from *Proc. Verb. Soc. Toscana Sci. Nat.*, 1898, 11, 104—107).—A finely crystalline, light ash-grey substance in a tourmaline-bearing granite from the Grotto d'Oggi, Elba, was found, on microscopical examination and chemical analysis, to be tourmaline. In the analysis, the loss on ignition represents water and silicon fluoride.

	SiO ₂	Al ₂ O ₃	FeO(MnO)	B ₂ O ₃	CaO	MgO	Na ₂ O	K ₂ O	Loss on ignition	Total
	38·30	37·54	12·20	7·47	trace	0·47	1·42	0·32	3·72	101·44

L. J. S.

Kieselguhr from County Antrim. By JAMES HOLMS POLLOK (*Sci. Proc. R. Dublin Soc.*, 1899, 9, N.S., 33—36).—Deposits of kieselguhr, resting on peat and covered only by vegetation, occur on both banks of the Lower Bann from Toome Bridge, where the river emerges from Lough Neagh, right down to Coleraine at the mouth. At Toome Bridge, the deposit is 4 feet thick. After cutting and drying in the sun, the material is pure white, porous and very light (sp. gr. of the mass, 0·5422). The material is probably now being deposited when the river overflows its banks, the diatoms, which are mostly cubical in shape, being brought down from Lough Neagh. Analyses gave:

	Soluble SiO ₂	Insol. SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	CaO	MgO	Alka- lis.	Organic matter, comb. water.	Mois- ture.	Total
I.	70·9	—	9·8	5·4	1·5	0·1	—	12·0	—	99·7
II.	57·12	15·89	8·55	2·09	1·14	0·83	0·28	7·71	6·39	100·00

L. J. S.

Illinois Gulch Meteorite. By H. L. PRESTON (*Amer. J. Sci.*, 1900, [iv], 9, 201—202).—This iron was found in 1899, 4 feet below the surface, in Illinois Gulch, Deer Lodge County, Montana. It weighs about 2435 grams, and measures 63 × 104 × 105 cm. No distinct figures are brought out by etching. A little troilite and

possibly some rhabdite are present. Analysis by Mariner and Hoskins gave:

Fe.	Ni.	Co.	Si.	P.	C.	Total.
92.51	6.70	0.16	trace	0.62	0.01	100.00
L. J. S.						

Composition and Properties of the Mineral Waters of Australasia. By ARCHIBALD LIVERSIDGE, WILLIAM SKEV, and G. GREY (*Rept. Australian Assoc. Adv. Sci.*, 1898, '7, 87—108).—A collection of all the available analyses that have been made.

L. J. S.

Physiological Chemistry.

Action of the Blood-gases on Breathing. By W. PLAVEC (*Pflüger's Archiv*, 1900, 79, 195—210).—The difference between the action of deficiency of oxygen and increase of carbon dioxide in the blood is greater than has been supposed. With small carbon dioxide tension in the blood, such as is obtained by breathing air containing 5 per cent. of the gas, there is only an action on the respiratory movements, but with greater tension the respiratory centre is greatly stimulated. The theory of Hermann, that the deficiency of oxygen raises the irritability of the centre to carbon dioxide, has no foundation; in fact, there is a progressive lessening of its excitability. The terminal inspirations of acute asphyxia are caused by the accumulation of carbon dioxide in the blood. The breathing in of this gas causes an increased rate of respiration, and its presence in the blood is the normal stimulus to produce breathing. W. D. H.

Respiration in the Frog. By J. ATHANASIU (*Pflüger's Archiv*, 1900, 79, 400—422).—The respiratory metabolism in the frog varies greatly with the time of year. The respiratory quotient is in the mean 0.77 in summer, and 0.95 in winter, but in the winter it may exceed unity. The high respiratory quotient apparently depends on reserve of oxygen in the tissues. W. D. H.

Nitrogenous Metabolism after Splenectomy. By LAFAYETTE B. MENDEL and HOLMES C. JACKSON (*Proc. Amer. Physiol. Soc.*, Dec., 1899; *Amer. J. Physiol.*, 1900, 3, iii—iv).—In view of the part supposed to be played by the spleen in uric acid formation, it was found that, in cats and dogs, removal of this organ does not lessen the normal output of uric acid, after diets of different kinds. The ability of the organism to form allantoin after ingestion of thymus or pancreatic tissue is in no way diminished. W. D. H.

Nutritive Value of Alcohol. By WIEBUR O. ATWATER (*Proc. Amer. Physiol. Soc.*, Dec., 1899; *Amer. J. Physiol.*, 1900, 3, xiii—xiv). Experiments on men show that alcohol serves the body as fuel, as

do fats and carbohydrates. 98 per cent. of the alcohol given was oxidised in the body, and the alcohol supplied about one-fifth of the total energy during rest, and about one-seventh during work.

W. D. H.

Digestion of Carbohydrates by Aplysia. By FRANZ RÖHMANN (*Chem. Centr.*, 1900, i, 50; from *Centr. Physiol.*, 13, 455).—The *Aplysia*, like the *Geophila*, live on the green portions of plants, and those found in the Bay of Naples principally consume the algæ, *Ulva lactuca*, which contains starch, and a pentosan which is soluble in water. By the action of an enzyme in the intestines, the starch is converted into dextrose. Although glycogen was not found in the intestines, the presence of a pentosan identical with that of the algæ was detected.

E. W. W.

Some Comparative Analyses of, and Digestion Experiments with, White and Whole-meal Breads. By OTTO ROSENHEIM and PHILIP SCHIDROWITZ (*Analyst*, 1899, 24, 227—234).—Analyses are recorded of ordinary white bread, ordinary whole-meal bread, and patent whole-meal bread; the figures relating to the two brown breads reveal no striking differences, and although the white bread was somewhat poorer in mineral phosphatic matter and total soluble constituents, its nitrogenous matter, or total, pure, and soluble albumin was about equal to that of the brown samples.

Digestion experiments (salivary, gastric + pancreatic, and pancreatic), conducted *in vitro*, did not accord with the popular belief in the superiority of the brown breads; in fact, white bread is superior as far as digestibility pure and simple is concerned.

L. DE K.

Plasmon. By HEINRICH PODA and WILHELM PRAUSNITZ (*Zeit. Biol.*, 1900, 39, 279—312).—Plasmon is a new preparation from the proteids of milk. The experiments here recorded, which were carried out on human beings, show that it is easily digestible and assimilable, and that its nutritive value is equal to that of meat.

W. D. H.

Assimilation of Iron. By EMIL ABDERHALDEN (*Zeit. Biol.*, 1900, 39, 193—270).—The numerous experiments here recorded on various animals relate principally to the estimation of hæmoglobin. They support the author's previous contention that the iron of inorganic compounds, of hæmoglobin, and of hæmatin in the food, is absorbed and utilised in the manufacture of hæmoglobin.

W. D. H.

Absorption in the Small Intestine. By OTTO COHNHEIM (*Zeit. Biol.*, 1900, 39, 167—172).—The main contention of the argument from the experiments recorded, which consisted chiefly in destroying the epithelium of the small intestine with hot water, is that the living cells play an important selective part in absorption. Hüber's contention that the act of absorption is the same in principle in living and dead animals is contested.

W. D. H.

Reduction of Cholesterol to Coprosterol in the Human Intestine. By PAUL MÜLLER (*Zeit. physiol. Chem.*, 1900, 29, 129—135).—Whether the reduction of cholesterol into coprosterol which Bondzynski showed occurred in the intestine is due to putre-

fective organisms or to the normal action of the digestive juices is a matter of doubt. By a pure milk diet, the putrefactive processes in the intestine are reduced to a minimum; under these circumstances, cholesterol is found unchanged in the fæces. The fact that cholesterol is found in meconium, the contents of the foetal intestine (Flint), also points to the bacterial origin of coprosterol. W. D. H.

Chemical Changes in the Developing Egg. By P. A. LEVENE (*Proc. Amer. Physiol. Soc.*, Dec., 1899; *Amer. J. Physiol.*, 1900, 3, xii—xiii).—The quantity of xanthine bases and nuclein compounds increases with the growth of the egg embryo. The importance of mineral salts increases also. The following table summarises the facts with regard to nitrogen; the numbers given are percentages:

Nitrogen.	Unfertilised eggs.	Eggs after fertilisation,		
		24 hours.	10 days.	19 days.
In mono-amino-compounds	21.10	21.37	22.72	0
In bases	12.07	25.10	12.48	28.25
In proteids	66.00	53.57	64.79	71.84

W. D. H.

Composition of Hen's Egg. By ADOLF JUCKENACK (*Chem. Centr.*, 1900, i, 304; from *Zeit. Unters. Nahr. Genussmittel.*, 1899, 905—913).—The quantity of phosphorus contained in the ash of yolk of egg does not represent much more than half the amount before incineration, for, owing to insufficiency of bases, a portion of the phosphoric acid is reduced during combustion; it is necessary, therefore, to add sodium carbonate and potassium nitrate before incinerating. An egg contains 0.455 per cent. of phosphorus, the white containing 0.031 and the yolk 1.279 per cent. Of the latter, 0.478 is present as distearyllecithin (5.42 per cent.), 0.345 as the compound of vitellin and distearyllecithin (3.93 per cent.), 0.178 as nucleins, and 0.278 as insoluble phosphates, glycerophosphoric acid or derivatives. The yolk contains 0.91 per cent. of cholesterol. E. W. W.

Chemical Composition of New-born Children. By WILLIAM CAMERER, jun., and FRIEDRICH SÖLDNER (*Zeit. Biol.*, 1900, 39, 173—192).—The total composition of three new-born children is given, and contrasted with that of human milk. W. D. H.

Chemico-physical Relations of Animal Juices and Tissues. By MAX. OKER-BLOM (*Pflüger's Archiv*, 1900, 79, 111—145).—The electrical conductivity reckoned for a unit column of 1 c.c. offering a resistance of 1 ohm is, at 25°, for defibrinated ox blood, 52.5 to 70.9; for ox-serum, 114.4 to 131.1; for defibrinated pig's blood, 44.5 to 51.5; and for pig's serum, 119.3 to 126.8; for a 0.7 per cent. solution of sodium chloride, it is 124.1, a number approximately equal to that of serum. By diluting blood or serum with distilled water, the conductivity increases much more quickly than that of a 0.7 per cent. solution of sodium chloride with the same amount of dilution. The degree of dissociation of the serum electrolytes is 0.65 to 0.76, and of the blood 0.34 to 0.45. Between 20° and 40°, the conductivity in-

creases with the temperature. No difference was found between arterial and venous blood. The conductivity depends partly on the electrolytes of the corpuscles. W. D. H.

Influence of Iodine, Sodium Iodide, and Iodothyron on the Circulation. By A. G. BARBÈRA (*Pflüger's Archiv*, 1900, 79, 312—318).—Largely polemical. Laudenbach has found that iodothyron has not the action on the circulation described by von Cyon. He, however, used Notkin's preparation, which appears to be very toxic, whilst von Cyon used Baumann's iodothyron. The latter lowers the blood pressure and the heart rate, whilst Notkin's preparation acts in the opposite way. Iodine and sodium iodide act like Notkin's preparation, stimulating the cardiac accelerators and vaso-constrictors, and depressing the inhibitory nerves of the heart and blood-vessels. W. D. H.

Infusion after Severe Hæmorrhage. By PERCY M. DAWSON (*Proc. Amer. Physiol. Soc.*, Dec., 1899; *Amer. J. Physiol.*, 1900, 3, xxviii).—After removal of large quantities of blood in dogs, infusion with isotonic solutions (normal saline with and without milk, Ringer's solution) was performed. A post-hæmorrhagic fall of red corpuscles continues for from four to eight days. This is not due to osmotic changes in the plasma, but to the low resistance of the remaining corpuscles. With regard to the post-hæmorrhagic leucocytosis which were noted, there is no evidence that the polymorpho-nuclears are formed from the lymphocytes, at any rate in the circulating blood. W. D. H.

Influence of Protoplasmic Poisons on Lymph Formation. By WILLIAM J. GIES and LEON ASHER (*Proc. Amer. Physiol. Soc.*, Dec., 1899; *Amer. J. Physiol.*, 1900, 3, xix—xx).—Experiments were made on dogs with quinine and arsenic. Quinine does not interfere with the usual influence of dextrose, but suppresses the action of leech extract. The action of dextrose as a lymphagogue therefore depends on physical factors, and of leech extract on physiological factors. The effect of sugar is not merely due to increased capillary pressure, for in a dog, after quinine and dextrose, the lymph flow continued for three hours after the animal's death. Arsenic increases the permeability of the vessel walls, but it hardly influences the flow of lymph. Starling's mechanical theory therefore fails. W. D. H.

Bile as a Solvent. By BENJAMIN MOORE (*Proc. Amer. Physiol. Soc.*, Dec., 1899; *Amer. J. Physiol.*, 1900, 3, xiv—xv).—Bile dissolves lecithin and cholesterol. It also dissolves soaps and free fatty acids. This power is due to the bile salts, and is increased by the presence of lecithin in solution. Cholesterol and soaps of calcium and magnesium are only slightly soluble in bile, but are more soluble when lecithin is present also. The sodium soaps are more soluble in bile than in water; the solution is less viscid when bile is present, and, on cooling, the soaps are precipitated in a granular form, not as a jelly. All these facts show the importance of bile in the digestion of fats. W. D. H.

Fat in Cartilage. By CESARE SACERDOTTI (*Virchow's Archiv*, 1900, 159, 152—173).—The fat in cartilage cells is constantly and

normally present. It increases in quantity with the physiological growth of, and diminishes with degenerative changes in, the cells, although in some cases of inanition the lessening of the cartilage fat is not perceptible.

W. D. H.

Hepatic Glycogen during Pregnancy. By ALBERT CHARRIN and A. GUILLEMONAT (*Compt. rend.*, 1900, 130, 673—675).—Experiments on guinea-pigs show that the hepatic glycogen increases during pregnancy, especially as full term approaches. This increase is more marked if sugar is supplied to the animals. The sugar eliminated by the urine is more considerable in gravid as compared with normal animals. The need of the animals for sugar is thus less during pregnancy, and the accumulated carbohydrate is believed to be used up later for the needs of lactation.

W. D. H.

Does Cellulose occur in the Shield of Sepia? By FRIEDRICH N. SCHULZ (*Zeit. physiol. Chem.*, 1900, 29, 124—128).—Ambronn (*Mitt. zool. Station Neapel*, 1890, 9, 475) states that besides chitin, the so-called *Os sepia* contains cellulose. This is stated to be an error.

W. D. H.

The Catechol-like Substance of the Suprarenals. By OTTO VON FÜRTH (*Zeit. physiol. Chem.*, 1900, 29, 105—123. Compare Abstr., 1899, ii, 115).—The active substance in the suprarenal bodies which produces the typical rise of blood pressure is termed *suprarenine*. It is believed to be a hydro-derivative of dihydroxypyridine of the composition $C_8H_7O_2N$ or $C_5H_9O_2N$. It may be readily separated as an iron compound, 0.000017 gram of which produces a rise of blood pressure. It differs in its reactions and composition entirely from Abel's epinephrine, which is stated to produce no effect on blood pressure. The suprarenals contain 0.01 per cent. of epinephrine, and from 0.1 to 0.17 per cent. of suprarenine. A very small contamination of the former with the latter would produce a rise of blood pressure.

W. D. H.

Deposits of Uric Acid Artificially Produced in Birds. By E. SCHREIBER and ZAUDY (*Pflüger's Archiv*, 1900, 79, 53—98).—In the course of Ebstein's investigations of the aetiology of gout, he succeeded with hens in producing deposits of urates artificially in the organs and tissues after ligature of the ureters, or injury to the kidneys produced by injection of chromates. These experiments having been called in question, the present work, carried out under Ebstein's supervision, consisted in repeating and confirming them. The deposits, partly crystalline, partly amorphous, were found in the blood, lymph, and among the tissue elements in various organs. Although the view is supported that the uric acid is the source of the irritation in gout, the actual deposition of the urates is considered to occur *post-mortem*, or at earliest in the *ante-mortem* death agony.

W. D. H.

Coagulable Proteids of Connective Tissues. By WILLIAM J. GIES and A. N. RICHARDS (*Proc. Amer. Physiol. Soc.*, Dec., 1899; *Amer. J. Physiol.*, 1900, 3, v).—In aqueous and magnesium sulphate

extracts of tendon, there are two coagulable proteids; one separates at 54—57°, the other at 73°. Elastic ligaments contain more proteid than tendon, and fractional heat coagulation indicates the existence of as many as five proteids; they also contain a large quantity of creatine.

W. D. H.

Glucoproteids of White Fibrous Tissue. By WILLIAM J. GIES and WILLIAM D. CUTTER (*Proc. Amer. Physiol. Soc.*, Dec., 1899; *Amer. J. Physiol.*, 1900, 3, vi).—The amounts of nitrogen and sulphur in the mucin obtained in lime-water extracts from the tendo Achillis indicate that there are several members of the group present, and that these are different from those in the tendon sheath. The osazone obtained melts at 182°, but a pure crystalline product was not isolated. Some experiments appear to indicate the possibility of the presence of glucosamine. The differences between mucins, mucoids, and chondro-proteids appear to depend chiefly on the proportions of proteid and acid radicles in them.

W. D. H.

Organic Phosphorus Compounds in Infants' Urine. By ARTHUR KELLER (*Zeit. physiol. Chem.*, 1900, 29, 146—184).—Children fed on mother's milk excrete less phosphorus than those fed on cow's milk. This is not entirely dependent on the amount of phosphorus in the food. Full particulars are given of experiments on numerous infants, healthy and sick, the amount of phosphorus being determined both in organic and inorganic compounds in the urine. The amount of organically combined phosphorus in three healthy children corresponds with 0.00218 to 0.0167 gram of phosphoric oxide, which is more in proportion to body weight than in adults; in relation to total phosphorus, from 0.5 to 9.9 per cent. is in organic combination; in adults, the number is from 1.6 to 4.8 (Oertel). These numbers do not run parallel to the total phosphorus or total nitrogen in either food or excreta. They are, however, parallel to the amount of phosphorus retained in the body. The amount is not influenced by the administration of sodium phosphate, but the organic phosphorus does not come exclusively from the food, but from organs rich in nuclein.

W. D. H.

Elimination of Sodium Cacodylate in the Urine after Administration by the Stomach. By HENRI IMBERT and E. BADEL (*Compt. rend.*, 1900, 130, 581—583).—Sodium cacodylate, when administered by ingestion in quantity amounting to 0.2 gram, has a marked effect in reducing the volume of urine eliminated for three or four days, although this soon returns to its normal amount. The greater part of the cacodylate is eliminated in the urine during the first twenty-four hours, and after this approximately the same minute quantity (0.003 gram) is eliminated each day for about a month, the elimination being then complete.

C. H. B.

Oxidation of Urine. Phenols and Indican. By S. COTTON (*J. Pharm.*, 1900, [vi], 11, 59—61. Compare *Abstr.*, 1899, ii, 780).—The oxidation product of indican, the formation of which is used as a test for this substance in urine, may be obtained from urine as follows: The urine is distilled with 1/20th of its weight of nitric acid until 40

per cent. has distilled over, the distillation being effected, as far as possible, out of contact with air. The solid carbonaceous residue in the flask is collected and treated with light petroleum to remove benzoic acid, &c., and then extracted with chloroform, which dissolves out the oxidation product of indican, and on evaporation yields it in the form of coloured, prismatic crystals.

The first portion of the distillate, obtained as above, contains benzoic acid, and the latter portions, a phenol derivative which forms a red crystalline potassium salt.

H. R. LE S.

Physiological Action of Tellurium Compounds. By WILLIAM J. GIES and L. D. MEAD (*Proc. Amer. Physiol. Soc.* Dec., 1899; *Amer. J. Physiol.*, 1900, 3, xx—xxi).—In dogs, small doses (0.1 gram daily) of tellurous oxide, sodium tellurite, and tellurium tartrate have no effect on metabolism. Tellurium is eliminated in the urine and fæces, and the odour of methyl telluride in the expired air is pronounced. Larger doses (0.2 to 0.5 gram) cause violent vomiting, disintegration of the gastric mucous membrane, interference with the secretion of hydrochloric acid, and regurgitation of bile. Under 1 per cent. of tellurium tartrate and sodium tellurite does not hinder artificial peptic or tryptic digestion. When tellurium compounds come in contact with tissue cells, reduction to the metallic state occurs, although tellurium itself is soluble in the body juices. Thus tellurium was recovered from liver, kidneys, bile, and brain, but most from the tissues about the point of injection.

W. D. H.

Behaviour of Chitosamine [Glucosamine] Hydrochloride in the Animal Organism. By THEODOR R. OFFER and SIGMUND FRÄNKEL (*Chem. Centr.*, 1900, i, 211; from *Centr. Physiol.*, 13, 489—491).—The urine of men or dogs fed with glucosamine hydrochloride showed distinct reducing properties and was dextrorotatory. By determining the rotatory power, it was found that when doses of 10—20 grams were administered to dogs *per os*, 20 per cent. of the glucosamine hydrochloride was excreted in the first seven hours, and that after this time the urine became optically inactive. Similar results were obtained by subcutaneous injection. Glucosamine may be separated from the urine as the benzoate.

E. W. W.

Study of the Relationship between the Chemical Constitution of Alkylated Alkaloids and their Physiological Action. By WLADIMIR ROSENSTEIN (*Compt. rend.*, 1900, 130, 752—755).—The following alkaloid salts, basic cinchonine hydrochloride, and the hydrochlorides of methylcinchonine, dimethylcinchonine, cinchotoxine and methylquinine, produce tetanic and epileptic convulsions, whereas the salts of the corresponding quaternary bases, namely, cinchonine and methylcinchonine methochlorides, dimethylcinchonine benzochloride, cinchonine dimethochloride, and quinine and methylquinine methiodides have a paralysing action; moreover, the toxic effect of the latter series is always much greater than that of the former.

No definite relationship can be traced as to effect of alkylation on the physiological action of the alkaloid; cinchotoxine and its

N-methyl derivative, methyleinchonine, have the same effect, whereas methylquinine differs from quinine in being a highly poisonous base. The curarising action of the second series of salts seems to be due to the molecular configuration peculiar to quaternary bases.

G. T. M.

Suprarenal Extracts. By BENJAMIN MOORE and C. PURINTON (*Proc. Amer. Physiol. Soc.*, Dec. 1899; *Amer. J. Physiol.*, 1900, 3, xv, xvi—xvii).—In the dog, injection of extracts of suprarenal medulla in doses varying from 0.24 to 24 millionths of a gram per kilo. of body weight produces marked results. The minutest doses produce a fall instead of a rise of blood pressure. This is considered to be due to the action of the same active substance, not to admixture with a second material. The results show that any activity possessed by the substances hitherto isolated from the suprarenal may be explained by slight contamination with the unaltered active principle. In separating the active substance, the use of alkali should be avoided. The presence of the chromogen must not be taken alone to indicate the presence of active material. A new colour reaction of the chromogen is described, namely, dilute ferric chloride after excess of zinc acetate gives an evanescent, deep violet colour, which, in strong solutions, leaves a violet precipitate.

W. D. H.

A Depressor Substance in the Suprarenal Gland. By R. HUNT (*Proc. Amer. Physiol. Soc.*, Dec., 1899; *Amer. J. Physiol.*, 1900, 3, xviii—xix).—After epinephrine has been removed from an aqueous extract of suprarenal by means of benzoyl chloride, a substance remains which produces a fall of blood pressure. By both chemical and physiological properties, this substance is found to be choline. Extracts of sympathetic ganglia and brain contain choline also.

W. D. H.

Mucin. By I. LEVIN (*Proc. Amer. Physiol. Soc.*, Dec., 1899; *Amer. J. Physiol.*, 1900, 3, xxix—xxx).—Thyroidectomy causes auto-intoxication from the accumulation of mucin in the blood. Injection of mucin in sodium carbonate has no effect on healthy rabbits, but is fatal to those without a thyroid. In dogs, it causes a fall of blood pressure due to its action on the vasomotor centre.

W. D. H.

Metabolism in Pernicious Anæmia. By WACLAW VON MORACZEWSKI (*Virchow's Archiv*, 1900, 159, 221—247).—Observations were made on four patients suffering from pernicious anæmia. In the simple anæmia, a noteworthy feature of the metabolism is a retention of chlorine. From the cases now recorded, the characters of the metabolism are so marked as to assist diagnosis. They are, a relatively large excretion of chlorine, an absolute loss of calcium, and a small excretion of both nitrogen and phosphorus.

W. D. H.

Multiple Amyloid Tumours in the upper Air Passages. By PAUL MANASSE (*Virchow's Archiv*, 1900, 159, 117—136).—Some cases of multiple tumours in the upper air passages are recorded, with full clinical and microscopical details. The substance of the tumours, which, in an early stage, appeared to be sarcomatous, was later found, from

its microscopic appearance and reaction with iodine, to be amyloid, or lardacein. From the history of the cases, and the examination after death, it is regarded as probable that the amyloid substance is formed within the lymphatic vessels and canaliculi, and that the infiltration of the connective tissue is secondary to this.

W. D. H.

Occurrence of Lactic Acid in the Animal Organism in Reference to Arsenical Poisoning. By KURATA MORISHIMA (*Chem. Centr.*, 1900, i, 45; from *Arch. exp. Path. Pharm.*, 43, 217—244).—Sarcoplactic acid occurs in the liver of all animals, and is also found in the kidneys, the coat of the stomach, and the blood. After death, the quantity of lactic acid in the liver increases as the glycogen decreases, fermentation lactic acid, however, being mainly formed. In cases of poisoning by arsenious oxide, the consequent rapid disappearance of glycogen in the liver is accompanied by the formation of a large quantity of paralactic acid in this organ, and also in the blood. Arsenical poisoning also causes an even larger increase of lactic acid in the kidneys than in the liver.

E. W. W.

Toxicology of Potassium Chlorate. By S. J. MELTZER (*Proc. Amer. Physiol. Soc.*, Dec., 1899; *Amer. J. Physiol.*, 1900, 3, ix—x).—Potassium chlorate does not cause death by changes in the blood. Death often supervenes before the blood is altered, and the formation of methæmoglobin within the vessels is comparatively harmless. Death results from paralysis of inspiratory muscles. Intracerebral injection shows it is a poison to nerve-cells, first exciting, then paralyzing them.

W. D. H.

Chemistry of Vegetable Physiology and Agriculture.

Fermentation of Yeast. By CARL J. LINTNER (*Chem. Centr.*, 1900, ii, 54; from *Centr. Bakt. Parasit.*, 5, ii, 793—800).—Chlorides check the fermentation of yeast, whilst the action of sulphates depends on the base. Zinc, magnesium, and ferrous sulphates, and potassium hydrogen phosphate promote the fermentation, whilst copper, and, still more, manganese sulphate, disodium phosphate, ammonium salts, and perhaps nitrates retard it. Saturated, and in some cases supersaturated, solutions were employed.

The fermentation of yeast diminishes gradually, as the reserve substances are consumed. By adding sodium sulphate, which induces vigorous fermentation, to yeast, it would be possible to ascertain whether the yeast is fresh, or whether it has been kept for some time; but this is not thought to be of practical importance.

The effect of salts may be due to abstraction of water, by which the plasma would be stimulated; excessive abstraction of water (by chlorides) would act deleteriously.

N. H. J. M.

Formation of Alcohol in the Putrefaction of Proteids free from Carbohydrates. By DIOSCORIDE VITALI (*Chem. Centr.*, 1900, i, 141—142; from *Boll. Chim. Farm.*, 38, 729—734).—Alcohol was found amongst the products formed by allowing horse muscle, from which the fat and sugar had been completely removed, to putrefy in presence of water at 28—32° from July to December. Blumenthal and Mayer (*Abstr.*, 1899, i, 968) have observed the formation of a hexose from albumin, and the glucoproteids or compounds of the simpler proteids, such as albumin or globulin with carbohydrates, also yield sugars which may be fermented. According to Gautier and Étard (*Abstr.*, 1882, 1115), the putrefaction and fermentation of muscular tissue takes place in two periods, an acid reaction obtaining in the first period, and an alkaline reaction in the second; the formation of alcohol takes place in the latter period. The bacteria which cause putrefaction are also capable of producing alcoholic fermentation. Experiments have been made with mucin, a glucoprotein found in considerable quantities in snails; the fresh aqueous extract was neutral, but on keeping became, first, acid, then, after a time, again neutral, and finally, in 2—3 months, acquired a faint alkaline reaction. True putrefaction had not, however, commenced, and consequently alcohol had not been formed. E. W. W.

Acetic Bacteria. By W. HENNEBERG (*Bied. Centr.*, 1900, 29, 66—67; from *Centr. Bakt. Parasit.*, 4, ii, 14, 67, and 138).—In addition to the two new varieties previously described (*Bied. Centr.*, 28, 647), a third (*Bacterium acetigenum*) has been found.

As regards temperature, it was found that in the case of five varieties (excluding *B. acetigenum*), the production of acetic acid is very slight at 33°, but is considerable at 26—29°, and (with the exception of *B. acetosum*) at 15° again very slight.

The degree of acidity produced, under conditions as favourable as possible, by the different varieties was as follows: *Bacterium oxydans*, 2; *B. acetigenum*, 2.72; *B. acetosum*, *B. aceti*, and *B. Kützingianum*, 6.6; and *B. Pasteurianum*, 6.2 per cent.

The highest percentage of alcohol in which acetic acid can be produced varies a good deal. The limit is lowest in the case of *B. acetigenum* (less than 5 per cent.); with *B. oxydans*, it is 7; with *B. Kützingianum*, and *B. Pasteurianum*, 9.5; and with *B. acetosum* and *B. aceti*, 11 per cent. None of the six varieties develops in beer to which 3—6 per cent. of acetic acid has been added.

N. H. J. M.

Effect of different Substances on the Curdling of Milk. By THOMAS BOKORNY (*Bied. Centr.*, 1900, 29, 62—65; from *Milchzeit.*, 1898, No. 49, 769).—Certain poisons, such as 0.01 per cent. solutions of hydroxylamine hydrochloride, formaldehyde, and menthol, which act strongly on putrefying bacteria, have no, or very little, effect on the lactic acid bacillus. A number of experiments were made in which various substances were added to milk, which was then kept at the temperature most favourable to curdling (26—27°). Milk alone curdled in 24 hours. In the following summary of results, the time required for curdling is given after each substance. Oil of turpentine

(1 : 75000), 48 hours; menthol (0.01 per cent.), 48 hours; eugenol (0.005 per cent.), 24 hours; cinnamaldehyde (0.005 per cent.), 24 hours; *p*- and *o*-hydroxybenzaldehydes (0.05 per cent.), after 48 hours; *p*- and *o*-hydroxybenzoic acids (neutralised, 0.05 per cent.), within 48 hours; *p*- and *o*-cresols (0.05 per cent.), 48 hours; paraldehyde (0.1 per cent.), 24 hours; salicylaldehyde (0.1 per cent.), 48 hours; carvol (0.05) and cuminaldehyde (0.005 per cent.), 24 hours; salicylic acid (0.2 per cent.), 3 days; heliotropin (0.1 per cent.), 24 hours; formaldehyde (0.002 per cent.), 24 hours; (0.01 per cent.), 3 days; (0.1 per cent.), no curdling in 6 days.

Silver nitrate (0.001 per cent.), 48 hours; (0.01—0.1 per cent.), 4 days; (0.2 per cent.), no curdling in 6 days; hydroxylamine hydrochloride (0.1 per cent.), 48 hours; boric acid (0.1—0.2 per cent.) has scarcely any appreciable effect according to Lazarus. Sodium carbonate (0.3 per cent.), no effect (Lazarus in *König's Nahrungsmittel*, 2, 244). Calcium hydroxide (0.15 per cent.) has no effect, and borax (0.4 per cent.) very little effect on bacteria (Lazarus). Hydrogen peroxide (0.1 and 1.0 per cent.), 3 days.

N. H. J. M.

Denitrification and Fermentation. By KURT WOLFF (*Chem. Centr.*, 1900, i, 52—53; from *Hygien. Rundsch.*, 9, 1169—1172. Compare this vol., ii, 98).—The bacteria employed in these experiments were four of the typhus-like bacilli (including *B. coli commune*, and Löffler's mouse typhus bacillus), and two hay bacilli (one apparently *B. Filtzianus*, from ginger root, the other from meal). All the bacilli reduced nitrates to nitrites in 1 per cent. dextrose broth containing 0.05—0.23 per cent. of potassium nitrate; but the extent of the reduction varied very much with the different bacilli; the coli-like bacilli reducing least, the hay bacilli the most, nitrate. Only one of the latter (of all six bacilli) can be compared with the real denitrifying organisms. The strength of the sugar solution was without influence, but the amount of nitrate present had a decided effect; an excess of nitrate checks fermentation, without, however, otherwise disturbing the functions of the bacilli; and complete disappearance of nitric nitrogen can only take place simultaneously with fermentation.

It is concluded that denitrification is not due to the direct action of the microbes, but that the products of fermentation reduce nitrates to nitrites and eventually convert them into carbonates.

Any fermentation of sugar, by whatever microbes it is caused, will, it is believed, destroy nitrates when present, and denitrification can only take place in presence of substances which yield denitrifying products of metabolism.

N. H. J. M.

Inoculation with Nitragin. By BERNHARD FRANK (*Landw. Versuchs.-Stat.*, 1899, 51, 441—445).—At the suggestion of the Prussian Agricultural Department, pot and field experiments with nitragin were made in 1896—1897, at twelve Experiment Stations. Positive results were only obtained at four of the twelve. The negative results are attributed to there being sufficient abundance of leguminous nodule bacteria already in the soil.

It is, however, pointed out that negative results were obtained on uncultivated land where the application of inoculating soil had proved to be at once effective. In such cases, the failure of nitragin is thought to be due to the cultivations being weak, and it is suggested that if the gelatin of nitragin were to be replaced by some substance more similar to the natural media of the nodule bacteria, better results might be obtained.

N. H. J. M.

How can the Action of Nitragin be Increased? By FRIEDRICH NOBBE and LORENZ HILTNER (*Landw. Versuchs.-Stat.*, 1899, 51, 447—462).—A reply to Frank (preceding abstract). It is stated, in the first place, that subsequent experiments made at the Prussian Experiment Stations in 1897—1898 have given more satisfactory results than the previous ones.

As regards the employment of gelatin, reference is made to earlier experiments, the results of which showed that gelatin cultivations were extremely vigorous. In some cases, inoculation of seedlings growing in absence of combined nitrogen, resulted in injury to the plant, owing to the vigour of the cultures; in presence of a little combined nitrogen, the gelatin cultures proved to be better than direct inoculation from nodules, production of active nodules being much quicker.

As regards the application of nitragin, dilution with distilled water may completely kill the bacteria, and even well-water may be injurious. It is thought that the extract of glycyrrhiza roots, known as "Lakritzen," might be advantageously employed. This could not, of course, be utilised in cultivating the bacteria, as they would all gradually become converted into the glycyrrhiza modification.

When seeds are inoculated, they should be allowed to swell before being sown. In the case of soil inoculation, the material may be added to a mixture of soil and finely cut leguminous hay; the mixture is sown over the land, not with the seed, but some weeks later, if possible in rainy weather.

N. H. J. M.

Action of Moulds on Arsenic and its Compounds. Biological Proof of the Presence of Arsenic. By RUDOLF ABEL and PAUL BUTTENBERG (*Chem. Centr.*, 1900, i, 428—429; from *Zeit. Hyg.*, 32, 449—490).—In the original paper, the part played by moulds in reference to arsenical poisoning caused by wall papers containing arsenic is discussed. Of the various microbes, the development of the moulds is least retarded by the presence of arsenious acid, and of 40 kinds which were examined, 10 were found to be capable of decomposing this acid and forming arsenical vapours. *Penicillium brevicarule* gave the best results (compare Gosio, *Abstr.*, 1897, ii, 381). The presence of 0.01, and often even of 0.001 mg. of arsenic may be detected by the arsenical odour produced by raising a strong culture of the mould in the presence of a soluble or insoluble substance containing arsenic. The conditions necessary, and the use of this method, in comparison with the ordinary chemical methods, are discussed in the original paper.

E. W. W.

Influence of the Temperature of Liquid Hydrogen on the Germinative Power of Seeds. By SIR W. THISELTON-DYER (*Proc. Roy. Soc.*, 1899, 65, 361—368. Compare Brown and Escombe, *ibid.*, 62, 161).—Various seeds which had been cooled to -250° , in one case in a vacuum, in another case by immersion in liquid hydrogen, showed no alteration in appearance, and germinated well. The question whether the temperature of the seeds actually reached that of the liquid hydrogen is discussed; in the case of the seeds immersed for more than six hours, there would seem to be no room for doubt.

N. H. J. M.

Changes in the Organic Constituents of the Seed during Germination. By GUSTAVE ANDRÉ (*Compt. rend.*, 1900, 130, 728—730. Compare this vol., ii, 159).—The amount of total nitrogen present in the seedling of *Phaseolus multiflorus* from the commencement of germination to the period at which the dry weight of the young plant is again equal to that of the seed is fairly constant.

On extracting the seedling with dilute acetic acid, the asparagine passes into solution as ammonium aspartate; the extract is rendered alkaline and distilled, the ammonia evolved being a measure of the asparagine present in the seedling; acetic acid also dissolves other amides which are not affected by the alkali. The amounts of asparagine and soluble amides attain their maxima when the dry weight of the seedling reaches its minimum; from this stage onwards, it appears that the soluble amides are utilised in the production of the insoluble proteid material of the young plant.

The soluble carbohydrates are extracted with warm 60 per cent. alcohol, hydrolysed by dilute acid, and estimated as reducing sugar; the amount of these substances is greatest in the seed and decreases continuously during germination.

The quantity of starch and hydrolysable cellulose diminishes rapidly during germination; on the other hand, the proportion of non-hydrolysable cellulose increases greatly, and when the seedling has regained its original weight, the increase is twofold. At the close of the period under examination, the amounts of cellulose and mineral constituents increase very rapidly, and there seems to be an intimate relation between the development of cellulose and the absorption of lime and silica. The analytical results are exhibited in tabular form.

G. T. M.

Digestion of the Reserves in Seeds during Germination and their Assimilation by the Seedlings. By PIERRE MAZÉ (*Compt. rend.*, 1900, 130, 424—427. Compare Abstr., 1899, ii, 607).—The production of alcohol and carbon dioxide in germination indicates that the weight of a plant just after germination, from an amylaceous seed, should represent about half the loss in the cotyledons. As germination proceeds, the relation should diminish, since there is also a loss due to construction in addition to the increasing loss due to maintenance. In accordance with this view, it was found that in the germination of peas and haricots, the relation of the weight lost by

the cotyledons to the weight of the seedlings was about 2 after 5—6 days, and increased to 2·3—2·4 at the end of 15—20 days.

Oleaginous seeds, or seeds with mixed reserves, give totally different results. The amount of carbon dioxide given off in 8 days was, however, about the same for *Arachis*, maize (which contain respectively 53·7 and 4·8 per cent. of ether extract), and haricots. It is thought that the conversion of fatty acids into sugar does not depend on the nature of the acid (compare Maquenne, Abstr., 1899, ii, 171); in the case of some oleaginous seeds, the sugar is utilised in constructing or maintaining the cells as soon as it is formed. The digestion of the oil in *Arachis* is thus comparable with that of starch in haricots or peas. *Ricinus*, on the other hand, accumulates sugar, and thus resembles the *Gramineæ*.

The transformation in oily seeds of the group CH_2 into $\text{CH}\cdot\text{OH}$ seems to be as general as the degradation of starch; it is shown to be due to a diastase.

N. H. J. M.

Accumulation of Asparagine in Leguminous Plants cultivated with Insufficient Light. By ÉMILE BRÉAL (*Ann. agron.*, 1900, 26, 5—19. Compare Prianischnikoff, Abstr., 1899, ii, 787).—It was found that when lupins were grown with insufficient light there was an accumulation of asparagine during the last months of the year, the dry matter of the stems and roots (when the plants were 25 cm. high) containing as much as 50 per cent. of asparagine. The nitrogen of the dry matter was 8 per cent., 6 per cent. being in the form of asparagine.

At the time when the stems had reached the length of 20 cm., the plants were still green. The dry matter of the plants weighed less than that of the seeds, and the loss amounted to 36 per cent.

Blue lupins were grown in nutritive solutions containing minerals alone and minerals with potassium humate. By the time the stems were 15 cm. long, the plants without humate had lost 31 per cent. of the dry matter of the seed, whilst those with humate lost 27 per cent.

Subsequent experiments with blue lupins grown in better light showed a gain in weight of dry matter, instead of a loss, and the percentage of asparagine was 4 to 15 in the dry matter.

Lentils, without the cotyledons, grown in solutions of starch, caused a loss of starch in the solutions, and the plants developed better when supplied with starch in addition to minerals than with minerals alone; white lupins were much benefited by potassium humate (compare this vol., ii, 35).

N. H. J. M.

Carbohydrates in the Reserve Material of Lucerne and Fenugreek Seeds. By ÉMILE BOURQUELOT and HENRI HÉRISSEY (*Compt. rend.*, 1900, 130, 731—733. Compare Abstr., 1899, i, 839 and 840).—The pulverised seeds of lucerne are macerated in a solution of lead acetate; after removing the excess of lead from the extract by oxalic acid, the carbohydrate present in the filtrate is precipitated by the addition of alcohol. The product is optically active; $[\alpha]_D + 84\cdot26^\circ$ (compare Müntz, Abstr., 1882, 709); on hydrolysis with dilute sulphuric acid at 110° , it yields a mixture of mannose (Abstr., 1899, ii, 817) and galactose; the carbohydrate is accordingly

a mannogalactan. A similar substance is also obtainable from the seeds of fenugreek. The two carbohydrates differ somewhat in composition and properties, but are both hydrolysed by seminase, with the production of reducing sugars.
G. T. M.

Presence of Dextrose and Lævulose in Beet Leaves. By LÉON LINDET (*Ann. agron.*, 1900, 26, 103—113. Compare Brown and Morris, *Trans.*, 1893, 63, 604; Maquenne, *Abstr.*, 1896, ii, 328; and Lobry de Bruyn and Alberda van Ekenstein, *ibid.*, i, 116).—The different parts of new leaves on beet developed in darkness, as well as in presence of light, were separated, the juice expressed, and the sucrose, dextrose, and lævulose determined. Determinations were also made in normal leaves from the beginning of July to the beginning of October, and in the large and new leaves at different dates from July 17—26.

In the case of etiolated leaves, sucrose is withdrawn from the roots and inverted. Respiration in the leaves is feeble, whilst the production of cellulose is active; in every case, the amount of lævulose is less than that of dextrose. Analogous results were obtained with roots from which the leaves had been removed, and which produced fresh leaves under the influence of light.

As regards the amounts of dextrose and lævulose in the different parts of the leaves, the results showed relatively less dextrose in the parts in which respiration is least active. Comparing the new and the old leaves on the same roots, the new leaves invariably contained relatively less lævulose to dextrose than the old ones; and the question arises whether the better utilisation of lævulose by the plant is not correlative with the production of vegetable tissue (compare Durin, *Ann. agron.*, 1876, 220). It would seem that the vegetable cell selects each sugar for a different function. Certain yeasts attack lævulose in preference to dextrose, others, dextrose rather than lævulose.
N. H. J. M.

Ash of a Cocoanut. By F. BACHOFEN (*Chem. Zeit.*, 1900, 24, 16).—The husk, inner shell, kernel, and milk yielded respectively 1.63, 0.29, 0.79, and 0.38 per cent. of ash.

Each of the ashes were fully analysed, and the results are communicated in tables. The ashes of the inner shell and kernel are richest in phosphoric acid and potassium.
L. DE K.

Plasmolysis. Determination of the Toxicity of Alcohols. By ALB. J. J. VANDEVELDE (*Chem. Centr.*, 1900, i, 481; from *Hand. v. III. Vlammsch Nat. Geneeskündig Congres. Antwerp*, 1899).—The poisonous effects of various alcohols have been measured by experiments on the cells of the red onion, which are rich in anthocyanin and readily exhibit plasmolysis. The poisonous nature of the monohydric alcohols increases with the molecular weight, thus amyl alcohol is about twice as poisonous as isobutyl alcohol, and much more poisonous than ethyl alcohol. Normal propyl alcohol is more poisonous than isopropyl alcohol. The aqueous solutions of the alcohols are usually about twice as poisonous as the alcohols themselves. The older cells withstand the action of the alcohols better than the younger.

E. W. W.

Toxic Action of a Series of Acids, and of their Sodium Salts on *Lupinus Albus*. By RODNEY H. TRUE (*Amer. J. Sci.*, 1900, [iv], 9, 183—192).—Toxic action may be due to the anions, the cations, or the undissociated molecules. In the case of hydrochloric, hydrobromic, nitric, and other inorganic acids, the anions are only slightly toxic compared with the H^+ ions; the toxic value of the sodium salts of these acids is low. In the case of organic acids, the undissociated molecules have considerable toxic action, often exceeding that due to the H^+ ions; in cinnamic acid solutions, for example, the undissociated molecules are credited with 77 per cent. of the total toxic action; the anions of organic acids have in general a low toxic value. J. C. P.

Cultivation of Wheat and Oats at Grignon. By PIERRE P. DEHÉRAIN (*Ann. agron.*, 1900, 26, 20—33. Compare Abstr., 1899, ii, 243).—The results of experiments with large and small wheat grain showed that the larger seeds gave a decidedly greater yield, but the difference was not so marked as might be expected from previous results. Of greater importance is the place of wheat in a rotation, and at Grignon a clover crop was found to be a bad preparation for wheat, perhaps owing to the abstraction by the clover of water from the subsoil.

As regards the best place for oats in a rotation, no very definite conclusion is drawn from the results of the experiments. The greatest yield was obtained after beet, but to grow oats after beet would put wheat after clover, which is undesirable. If potatoes are grown in the place of roots, it is better to grow oats after wheat than after barley, especially if the wheat is succeeded by vetches to be ploughed in. N. H. J. M.

Experiments on Meadows. By BRIGHETTI (*Bied. Centr.*, 1900, 29, 23—26; from *Staz. sper. agrar. ital.*, 1898, 31, 620).—Analyses were made of the herbage from 15 meadows on alluvial soil in Ferrara. The results of botanical separations into gramineous, leguminous, and miscellaneous herbage are also given.

The percentage of proteids is highest in hay containing the most leguminous and leafy plants. The *Leguminosæ* predominated under the influence of phosphatic manures, whilst the unmanured land, and that which received compost, produced the most grass.

N. H. J. M.

Vegetation of some Fodder Plants. By MONVOISIN (*Ann. agron.*, 1900, 26, 77—103. Compare DehéRAIN and Bréal, Abstr., 1882, 419; DehéRAIN and Meyer, *ibid.*, 1883, 493; and Villard and Bœuf, *ibid.*, 1898, ii, 181).—Experiments were made with a number of plants to ascertain whether the laws found by DehéRAIN and Bréal in the case of annuals also hold good in the case of plants of longer life.

The amount of root is always high in relation to the stems; it is greatest at the beginning, and is always greater than in the case with annuals.

When the period of maturation has passed, there is a distinct loss

of dry matter. The roots contain more ash than the stems; the maximum amount of ash in the entire plant is not at the beginning of vegetation, or at the flowering period, but between the two. Plants of more than annual growth contain more ash than annuals.

The maximum amount of total nitrogen, like that of ash, was found towards the end of April; afterwards the amounts diminish regularly. Leguminous roots contain more nitrogen than those of the *Gramineæ*. Nitrogen as non-proteid is relatively most abundant at the beginning of vegetation.

N. H. J. M.

Analyses of Norwegian Hay. By FR. WERENSKIOLD (*Bied. Centr.*, 1900, 29, 19—22; from *Tids. Norsk. Landbr.*, 1899, 6, 35—43 and 82—85. Compare Abstr. 1897, ii, 187).—Further analyses of hay from various parts of Norway. Hay from peat land in Vegusdal, where cattle suffer a good deal from weak bones, contained only 2·86—3·82 per cent. of ash; its injurious effect may, however, be partly due to the small amounts of digestible proteids (three samples out of five contained only 1·08—2·26 per cent.).

Analyses of a number of single plants from Nordland are given.

N. H. J. M.

[Experiments on Sugar-cane in Hawaii.] By WALTER MAXWELL (*Chem. Centr.*, 1900, ii, 357).—Phosphates had practically no effect in increasing the yield of sugar, whilst potash and nitrogen increased the yield by 14 per cent. when employed singly and still more when employed together.

Analyses of the soil and of different parts of the plants are given in the original paper (Honolulu, 1899).

N. H. J. M.

Cultivation of Blue Lupins. By PIERRE P. DEHÉRAIN and E. DEMOUSSY (*Compt. rend.*, 1900, 130, 465—469. Compare this vol., ii, 238).—Blue lupins cannot themselves utilise elementary nitrogen. They may, however, grow normally when their roots are free from nodules; in this case, nitrogen is fixed by bacteria in the soil, associated with algæ (*Phormium autumnale* and *Ulothrix flaccida* were found in about equal amounts). Lupins also grow normally both in acid and in alkaline soil when provided with root nodules containing microbes which fix free nitrogen; in some cases, the nodule bacteria act as parasites, causing the plants to fail.

Arable soils do not generally seem to contain nodule microbes suitable for blue lupins; the microbes are, however, common in heath soil. Arable soil, can no doubt, be made available for blue lupins by inoculation.

N. H. J. M.

Manurial Experiments with Potatoes. By B. SJOLLEMA (*Bied. Centr.*, 1900, 29, 13—14; from *J. Landw.*, 1899, 47, 103).—Field experiments have been made on peat land at Groningen from 1881—1897, on potatoes alternated with cereals (generally oats). The greatest yield of potatoes (31,600 kilos.) was obtained with farm-yard manure, but the percentage of starch (14·25) was lower than with complete minerals and nitrate (31,500 kilos. with 16·15 per cent. of starch). Sodium nitrate (with complete minerals) gave better results than ammonium salts, both as regards total yield and per-

centage of starch. Complete minerals alone gave the highest percentage of starch (16·45), whilst the yield of tubers was 27,800 kilos.; with potash alone, the yield was 24,150 kilos., and the percentage of starch 16·2; with phosphoric acid alone, the yield was 9160 kilos., and the starch 15·5 per cent. Addition of nitrate and lime to phosphate and to potash respectively increased the yield of tubers considerably, but lowered the percentage of starch. With complete minerals, nitrate increased the production of tubers without very appreciably diminishing the amount of starch.

The unmanured plots gave 8900 kilos. of potatoes containing 14·8 per cent. of starch.

Farmyard manure continued to act for three years, whilst artificial manures acted as much as dung for at least one year.

N. H. J. M.

Influence of Chlorides and other Compounds present in the Crude Stassfurt Salts on the Composition and Yield of Potatoes. By B. SJOLLEMA (*Chem. Centr.*, 1900, ii, 360; from *J. Landw.*, 47, 305—307).—The injurious effect of Stassfurt salts on potatoes is attributed exclusively to the chlorides present. Potassium, sodium, and magnesium chlorides diminish about equally the percentage of starch, especially in varieties of potato rich in starch. The effect is very marked when 1250 kilos. of kainite are applied in the spring.

Potassium sulphate and “potash magnesia” applied to soils which require potash for potatoes are favourable rather than unfavourable to starch production. The tubers contain about the same amount of potash, whether applied as sulphate or as potassium salts containing chlorides.

The diminished production of starch under the influence of chlorides is partly due to the absorption of water being increased. The amount of potash in the dry matter of the tubers is then much higher than when potassium sulphate is employed, the excess of potash being in the form of chloride.

Soda, even when applied in large amounts, is not taken up by potatoes. Sodium and magnesium sulphates are not injurious, but seem to increase both the yield of tubers and the percentage of starch; they also reduce the amount of potash in the tubers.

Spring manuring with potassium salts containing much chloride diminishes the yield of potatoes, and still more the percentage of starch, the favourable effect of potash being considerably more than counterbalanced by the injury due to chlorides.

N. H. J. M.

Injurious Effect of Sodium Nitrate on the Growth of Sugar Beet. By JULIUS STOKLASA (*Chem. Centr.*, 1900, ii, 360—361; from *Zeits. Zucker-Ind. Böhm.*, 24, 131—146. Compare Sjollema, *Abstr.*, 1897, ii, 585; and Zaharia, *Abstr.*, 1899, ii, 799).—The toxic equivalent (expressed as fractions of the mol. weight in grams per 100 c.c.) of potassium perchlorate was determined for different plants at different periods of growth. For sugar beet, potassium perchlorate is not such a strong poison as copper and zinc sulphates, and sodium nitrate containing 2 per cent. of perchlorate has no effect on seed-

lings of sugar beet when the concentration did not exceed 1/10000 of the mol. weight (grams) per 100 c.c. It is thought that 200—500 kilos. per hectare of sodium nitrate containing 2 per cent. of perchlorate could be applied without injury to beet.

The toxic equivalents for rye, oats, and barley (or wheat) were found to be 1/10000, 1.5/10000, and 2/10000 respectively. Assuming the upper 20 cm. of soil to contain as little as 5 per cent. of water (which would only be in dry, summer periods), 100 kilos. of sodium nitrate with 1 per cent. perchlorate would give a concentration of 0.001 per cent., an amount insufficient to injure rye. With more sodium nitrate, or with a higher percentage of perchlorate than 1, rye is distinctly affected. For oats and barley (or wheat), the nitrate may contain 1.5 and 2 per cent. of perchlorate when the amount applied is 100 kilos. per hectare.

N. H. J. M.

Effect of Rain and of the Nature of the Soil on the Production of Crops. By AIMÉ PAGNOUL (*Bied. Centr.*, 1900, 29, 16—19; from *Ann. agron.*, 1899, 25, 83).—Pot experiments are described in which *Festuca pratensis* and incarnate clover were grown in light soil, loam, and calcareous soil respectively. One set of pots received rather less water than would have been the case if exposed to rain, whilst the second set received twice the amount given to the first. From the results, the following conclusions are drawn:

Gramineæ yield about three times, clover almost four times, as much produce in wet as in dry weather. The effect of the greater amount of water was greatest with loam, and least with calcareous soil. Loamy soil gave the smallest yield both of grass and clover, whilst the light soil (which contained 11.85 per cent. of calcium carbonate and 0.462 per cent. of phosphoric acid) gave the best yields.

The plants which received the smaller amount of water contained the greater percentage of dry matter, although the total dry matter was less. The percentage of nitrogen in dry matter was lowest in the plants grown in loam; the total nitrogen was almost twice as high in the case of the plants which received much water as compared with those which had the smaller amount of water.

A second cutting of *Festuca* gave similar results. Subsequently, the same amounts of water were given to all the plots, with the result that the yields became much more alike; the effect of the differences in the previous watering was, however, still noticeable, especially in the case of the loamy soil.

N. H. J. M.

Utilisation by Plants of the Potash Dissolved in the Water in Soil. By TH. SCHLÖSING, jun. (*Compt. rend.*, 1900, 130, 422—424. Compare Abstr., 1899, ii, 119).—The potash dissolved in soil has, like the phosphoric acid (*loc. cit.*) a considerable nutritive value for vegetation, notwithstanding its relatively small amount; the three or four million kilos. of soil, representing a hectare, contain 1, 2, or 5 kilos. of dissolved potash.

In experiments with maize grown in sand, it was found that a solution containing 7.5 parts of potash per million, in addition to

other minerals in suitable quantity, enabled the plants to grow normally, whilst with a solution containing the same amounts of other minerals, but only 1·8 per million of potash, very much less growth was obtained, and the plants produced no fruit. Maize plants can therefore thrive when they have to depend on solutions containing only some millionths of potash.

N. H. J. M.

Injury to Agricultural Land on the Coast of Essex by the Inundation of Sea-Water on November 29th, 1897. By THOMAS S. DYMOND and FRANK HUGHES (*Chem. News*, 1899, 80, 191—194).—A large area of land was rendered infertile by flooding with sea-water, which itself contained 2·7 per cent. of sodium chloride, or sufficient to cause plasmolysis; the soil which had been flooded contained, however, an amount of salt insufficient to produce that effect. The quantity varied with the character of the soil and period of flooding, but on an average amounted to 0·25 per cent. in the top soil, or 25 times more than the average amount in the soil from land not flooded; nevertheless, pot cultures showed that many plants could grow in the soil from the flooded land. Investigation showed that the infertility was due to the extermination of the earth-worm and to the clay having become more gelatinous, and the soil consequently rendered less pervious to water. This condition was attributable to an increase in the combined water of the clay which was accompanied by a reduction by $\frac{1}{5}$ th in the amount of lime, magnesia, potash, and soda. Although the total potash in the clay had been reduced from 1·12 to 0·84 per cent., the available potash had increased from 0·025 to 0·079 per cent.; the available phosphates had also increased in quantity. To restore the land, good cultivation, good draining to aid the washing out of the salt, manuring with lime, with nitrogenous manures, with long hay manure, and if phosphate is required, with basic slag, are recommended. Suitable plants for crops are mentioned.

D. A. L.

Field Experiments with Superphosphate and Basic Slag. By PAUL BAESSLER (*Bied. Centr.*, 1900, 29, 12—13; from *Ber. Agrik.-Chem. Versuchs-Stat. Köslin* for 1897, 113).—Barley and oats were manured with equal amounts of water and citrate-soluble phosphoric acid (as superphosphate and basic slag), in addition to kainite and nitrate. The soil was a humous, loamy, or slightly loamy, sandy soil containing 0·064—0·091 per cent. of phosphoric acid, of which 4 or 5 parts dissolved in 1 per cent. citric acid.

Owing to unfavourable weather, the results were very irregular. Taking all the results together, it is seen that 40 kilos. of phosphoric acid soluble in water increased the yield of grain by 223, and the yield of straw by 147, kilos. per hectare, whilst the same amount of phosphoric acid soluble in citric acid increased the yields by 183 and 278 kilos. respectively. With 60 kilos. of phosphoric acid per hectare, the increase of grain was 310 kilos. with water soluble, and 288 with citrate soluble phosphate, and the increase of straw 412 and 435 kilos.

The results do not confirm the opinion that basic slag must be applied in the autumn.

N. H. J. M.

Field Experiments with Potash-lime Manure and Fish Guano. By PAUL BAESSLER (*Bied. Centr.*, 1900, 29, 10—12; from *Ber. Agrik.-Chem. Versuchs-Stat. Köslin* for 1897, 120).—Experiments were made in which winter-rye and sugar-beet were grown in humous, sandy soil, manured with the same amounts of potash in the form of potash-lime manure* and kainite, in addition to superphosphate. There were also plots manured with superphosphate alone, and with fish guano. The effect of the two potash manures on rye was only slight, and was almost the same. The results of the superphosphate and fish guano showed that the effect of the latter depended mainly on the nitrogen it contained. In the case of sugar-beet, the potash manures had a decided effect on the leaf development and on the yield of roots, but the effect of the two manures was nearly the same.

The results of experiments on meadows, as well as those just described, showed that potash-lime manure is mainly of use as a potash manure.

N. H. J. M.

Importance of Poultry Manure. By R. ULRICH (*Bied. Centr.*, 1900, 29, 3; from *Fühling's Landw. Zeit.*, 1897, 627).—Pigeons, fowls, ducks, and geese produce yearly 2·5, 5·5, 8·5, and 11 kilos. of manure per head. The composition of the manure is as follows:

	Water.	Organic matter.	N.	P ₂ O ₅ .	Alkali salts.	Ash.
Pigeons	62	31—32	1·2—2·4	3·0—4·2	2·0—2·2	6—7
Fowls...	65	21—26	0·7—1·9	5·0	1·2—1·6	9—14
Ducks..	53	40	0·8	3·5	0·4	7
Geese...	82	14	0·6	0·9	3·1	4

The nutritive constituents are in a readily soluble and concentrated form, especially in the case of pigeon-dung, and must be employed with care. The manures should not be employed in dry weather, or on soil which is dried up; they should be mixed with water, and addition of sulphuric acid (30 lb. per cwt.) is recommended. They may be applied to roots and cabbages, &c., with advantage.

N. H. J. M.

Analytical Chemistry.

Perezone, a New Indicator for Alkalimetry. By MAURICE DUYK (*Chem. Centr.*, 1900, i, 60; from *Ann. chim. anal. appl.*, 1899, 4, 372).—Perezone (pipitzahoic acid), which exists to the extent of about 5 per cent. in the rhizomes of *Perezia adnata*, is an extremely sensitive alkalimetric indicator (compare Abstr., 1885, 805). A drop of a 5 per cent. alcoholic solution gives a feeble opalescence to

* This is a waste product from the manufacture of potash, and contains CaCO_3 , 41.8; K_2SO_4 , 7.7; CaO , 0.33; K_2O (as sulphate), 4.2 per cent., besides water (about 25 per cent.), Fe_2O_3 , Al_2O_3 , MgCl_2 , NaCl , and SiO_2 (*Bied. Centr.*, 1898, 27, 306).

distilled water, and the liquid becomes rose-coloured with traces of alkalis. Ammonia, aniline, pyridine, and alkaloids, carbonates, hydrogen carbonates, borates, and acetates behave as alkalis. The red liquid becomes colourless on adding mineral or organic acids, or carbon dioxide. Boric acid has an alkaline reaction, but after adding glycerol behaves as an acid. M. J. S.

Retention of Moisture by Asbestos. By GEORGE AUCHY (*J. Amer. Chem. Soc.*, 1900, 22, 46—47).—Some kinds of asbestos retain moisture with great tenacity, even after drying at 100°; on heating again over a blast, a loss of several milligrams may occur. It is therefore advisable to ascertain once for all the amount of water retained in a sample which is intended for use in a Gooch crucible. L. DE K.

Estimation of Water in Syrups and similar Products. By OSKAR MOLENDÁ (*Chem. Centr.*, 1900, i, 71—72; from *Oesterr.-ung. Zeit. Zucker-Ind. und Landw.*, 28, 621).—The author makes use of the reaction between water and calcium carbide, and measures the acetylene evolved. Scheibler's calcimeter is convenient for the purpose. Solutions stronger than 30 per cent. cannot be employed; those of 20—27 saccharimetric degrees are the most suitable. The syrup must therefore be diluted with water, and the amount of water added is best estimated from polarimetric observations of the original substance and the dilute solution. About 0.1 gram of the dilute solution is taken, and the formula $0.612 A/\text{subs.}$ in grams, in which A represents the percentage of calcium carbonate given by the calcimeter table as corresponding with the volume of gas, gives the percentage of water. Pure water gave an average result of 98.83 per cent., and sugar solutions of known composition gave differences averaging 2.56 per cent. M. J. S.

Estimation of Sulphur in Ores, Mattes, &c. By P. TRUCHOT (*Chem. Centr.*, 1900, i, 62; from *Ann. chim. anal. appl.*, 4, 374).—A gram of the finely powdered substance is rapidly heated in a covered beaker with 25 c.c. of concentrated nitric acid so long as red fumes are evolved. The liquid is cooled, twice warmed gently for 5 minutes with 1 c.c. of bromine, then evaporated on the water-bath almost to dryness, boiled with 15 c.c. of hydrochloric acid, diluted with 250 c.c. of water, filtered, and precipitated while boiling with barium chloride. M. J. S.

Estimation of Sulphur in Pig Iron and Cast Iron. By ADOLF RIEMER (*Chem. Centr.*, 1900, i, 61—62; from *Stahl. und. Eisen*, 1899, 19, 1064).—Wiborgh's method (*Abstr.*, 1886, 743) is utterly untrustworthy, indicating only about half the sulphur present. A rapid and exact method is to dissolve the metal in concentrated hydrochloric acid, and pass the evolved gases (after first washing with water) through ammoniacal cadmium acetate. An excess of standard iodine solution is added, the mixture acidified with hydrochloric acid, and the excess of iodine then titrated with thiosulphate. In very exact analyses, the cadmium sulphide precipitate should be collected and washed. M. J. S.

Estimation of Sulphur in Pyrites. By OLE. N. HEIDENREICH (*Chem. Zeit.*, 1900, 24, 15).—The author recently improved the estimation of sulphur in pyrites or burnt pyrites by reducing the ferric solution to the ferrous state by means of zinc before adding barium chloride (Abstr., 1899, ii, 517). Thiel has stated that the supposed accuracy of the results is only due to a fortunate compensation of errors (this vol., ii, 242). In reply, the author points out that Meineke has independently investigated the method and finds the results to be trustworthy (Abstr., 1899, ii, 518, 693).

L. DE K.

Estimation of Sulphur in Bitumens. By A. C. LANGMUIR (*J. Amer. Chem. Soc.*, 1900, 22, 99—102).—The author criticises the process recommended by S. F. and H. E. Peckham (this vol., ii, 44), and points out several sources of error. No precautions are taken to prevent absorption of sulphur compounds during the fusion with alkali nitrate and the subsequent slow evaporation of the dissolved mass with hydrochloric acid. The most serious objection is, that on precipitating the iron and aluminium by means of ammonia and expelling the excess of the latter by boiling, a portion of the sulphuric acid recombines with the iron. Finally, if the sulphuric acid is precipitated after removing the calcium with ammonium oxalate, there is a danger of obtaining a very impure barium sulphate, which is rendered still more probable by the presence of a large quantity of alkali chlorides.

Eschka's process, as described by Heath, is admittedly the best process for the estimation of sulphur in bituminous coals.

L. DE K.

Estimation of Alkali Persulphates and of Hydrogen Peroxide. By BRUNO GRÜTZNER (*Arch. Pharm.*, 1899, 237, 705—706).—About 0.3 gram of the *persulphate* is heated to boiling with 50 c.c. *N*/10 arsenious acid, and a few grams of aqueous potassium or sodium hydroxide, the whole digested for a little while, cooled, made faintly acid with sulphuric acid, treated with a large excess of sodium hydrogen carbonate, mixed with starch solution, and titrated with *N*/10 iodine solution. 1 c.c. *N*/10 $\text{As}_2\text{O}_3 = 0.0135$ gram $\text{K}_2(\text{SO}_4)_2$, 0.0119 $\text{Na}_2(\text{SO}_4)_2$, or 0.0114 $(\text{NH}_4)_2(\text{SO}_4)_2$. The error in the analyses quoted does not exceed ± 0.2 per cent.

Of a commercial sample of *hydrogen peroxide*, 10 c.c. are diluted to 100 c.c., and 10 c.c. of the dilute solution treated as is the persulphate in the method just described; 1 c.c. *N*/10 $\text{As}_2\text{O}_3 = 0.0017$ gram of hydrogen peroxide. A result was obtained 0.04 per cent. higher than by titration with permanganate. Sodium peroxide cannot be analysed in this way.

C. F. B.

Estimation of Ammonia and of Nitrogen. By ANTOINE VILLIERS and E. DUMESNIL (*Compt. rend.*, 1900, 130, 573—576).—The estimation of ammonia by titration is often inaccurate, because of the effect of ammonium salts on the indicator used, and better results are obtained by weighing the ammonia in the form of ammonium chloride. The ammonia is absorbed in an excess of dilute hydro-

chloric acid which has previously been found to leave no residue on evaporation, and the solution is concentrated in a porcelain dish over a small flame which heats only the bottom and not the sides of the vessel. When the liquid is reduced in volume to about 25 c.c., it is transferred to a small weighed conical flask, in which the evaporation is completed, the residue being dried at 105° . C. H. B.

The Phosphometer, an Apparatus for the Clinical Estimation of Phosphorus in Blood. By ADOLF JOLLES (*Chem. Centr.*, 1900, i, 486—487; from *Wien. Med. Woch.*, 1899, Nos. 46, 47).—The estimation is a colorimetric one, in which the yellow coloration produced by potassium molybdate in solutions of phosphates is used as a measure of the phosphate present. The intensity of the colour varies with the temperature, reaching its maximum at 80° . The comparison tubes are therefore observed in a cylindrical vessel surrounded by a water jacket, and are so arranged that three tubes (one of which contains the substance and the other two standards) can be simultaneously seen by light thrown upward from an oblique mirror below the cylinder. The substance is prepared by evaporating a measured quantity of the blood (0.1 c.c.) in a platinum crucible, fusing the residue with a mixture of sodium carbonate and potassium nitrate (3:1), and dissolving the fused mass in dilute nitric acid. The comparison solutions are prepared by dissolving 18.7324 grams of sodium pyrophosphate in 50 c.c. of nitric acid of sp. gr. 1.2 and diluting to a litre; from this solution, others are prepared containing 2, 0.2, and 0.02 milligrams of P_2O_5 per c.c. The potassium molybdate solution contains 8 grams of the salt in 50 c.c. of water and 50 c.c. of nitric acid of sp. gr. 1.2; for use, 1 c.c. of this solution is diluted to 20 c.c. M. J. S.

Simplified Method of Estimating Phosphoric Acid by Molybdate. By JOSEPH HANAMANN (*Chem. Centr.*, 1900, i, 488—489; from *Zeit. landw. Vers.-Wes. Oesterr.*, 3, 53).—By employing a molybdate solution containing more nitrates than the usual one, and precipitating at 40° , the precipitation of the phosphoric acid is complete in ten minutes, and the precipitate is of constant composition after gentle ignition, containing 3.94495 per cent. of phosphoric oxide. The molybdate solution is made by dissolving 100 grams each of ammonium molybdate and ammonium nitrate in 150 c.c. of ammonia of sp. gr. 0.91 and pouring the solution into a litre of nitric acid of sp. gr. 1.2. After boiling the solution, it is filtered into bottles of brown glass, and kept in a cool place. M. J. S.

Wagner's New Reagent for Estimating Soluble Phosphoric Acid in Basic Slag. By ADOLFO CASALI (*Chem. Centr.*, 1900, i, 62; from *Staz. sper. agrar. ital.*, 32, 486).—The use of citric acid for extracting the soluble phosphate from basic slag gives a much higher result than that obtained with the ammonium citrate more usually employed. In reporting the results of analyses, it should always be stated which reagent has been used. M. J. S.

Detection of Adulterations in Bone Superphosphate. By HENRI LASNE (*Chem. Centr.*, 1900, i, 72—73; from *Ann. chim. anal. appl.*, 4, 361).—The results of the estimations made should be

expressed in the form of ratios to 100 parts of phosphoric oxide present. The total phosphoric oxide and calcium oxide are first estimated. In normal bone, this ratio is 100:129—134. A higher ratio of calcium oxide points to the addition of either gypsum or mineral phosphate. Gypsum is sought for by the microscope. A deficiency of calcium oxide indicates addition of precipitated phosphate. Calcium chloride is also estimated. A ratio of 0.15 is compatible with purity; 0.3 points to the addition of gypsum, and a higher ratio is characteristic of precipitated phosphate. Addition of mineral phosphate raises the ratio of aluminium and insoluble matter (containing titanium) and also that of calcium fluoride (of which only traces are normally present), or, in the case of certain phosphates which are poor in fluorine, introduces manganese. Bone ash is best detected by partially precipitating with ammonia, collecting the precipitate, and treating it with dilute hydrochloric acid, when fragments of bone can be seen. The part of a normal bone-superphosphate insoluble in dilute hydrochloric acid seldom contains more than 0.1 of nitrogen per 100 parts of original substance; a greater proportion indicates addition of nitrogenous waste materials. The superphosphate itself should contain about 0.6 per cent. of nitrogen (see also this vol., ii, 167).

M. J. S.

Separation and Estimation of Arsenic and Antimony in Ores. By O. C. BECK and H. FISHER (*Chem. News*, 1899, 80, 259—261).—A critical examination and comparison of various known methods. The best results for arsenic were obtained by Pattinson's method (Abstr., 1899, ii, 56) of titrating the sulphide with iodine; weighing the sulphide gave results which were too high. Fischer's distillation method (Abstr., 1881, 195) gave good results, but, like Pearce's nitrate method (*Chem. News*, 1883, 48, 85), took too long; the latter, moreover, even when modified, gave low results. For antimony, Weller's method (Abstr., 1882, 1324) and Mohr's method gave fairly concordant results, whilst weighing the antimony as sulphide gave results too high, and as oxide, too low. Jannasch's modification occupied more time and introduced much sulphur, but gave higher results.

D. A. L.

Volumetric Estimation of Boric Acid. By ALFRED STOCK (*Compt. rend.*, 1900, 130, 516—517. Compare this vol., ii, 47).—In estimating boric acid by Jones's volumetric method (Abstr., 1899, ii, 322), it is essential that carbon dioxide should be absent; traces of this gas are most conveniently removed by boiling the solutions employed before titration; the removal of the gas by means of barium chloride is not to be recommended, because the barium carbonate produced interferes with the end point. The presence of salts of the alkali and alkaline earth metals does not affect the process; when iron and aluminium are present, their insoluble hydroxides are produced; the titration must, however, be performed in the presence of these substances, since the precipitate may contain variable quantities of borates; these salts are readily decomposed by the standard sodium hydroxide, and accurate results are obtained even under these conditions.

G. T. M.

The Accuracy of Jörgensen's Method for Estimating Boric Acid in Preserved Meat, and the Separation of Boric Acid from Borax. By ADOLF BEYTHIEN and HANS HEMPEL (*Chem. Centr.*, 1900, i, 63—64; from *Zeit. Unters. Nahr.-Genussmitt.*, 2, 842).—Jörgensen's method depends on the fact that a boric acid solution, rendered neutral to phenolphthalein by addition of alkali, becomes acid again on adding a sufficient quantity of glycerol, so that the boric acid can be titrated by an alkali which has been standardised by a boric acid solution of known value, under similar conditions as regards amount and concentration. The results are very satisfactory.

To estimate the boric acid in meat, the substance may either be extracted by warming for several hours with strong sodium hydroxide solution, and the extract evaporated and incinerated, or, more expeditiously and with little loss of accuracy, by direct incineration of the meat itself after carefully and thoroughly saturating it with a large excess of an alkaline solution. The ash, in either case, is dissolved in 50 c.c. of dilute sulphuric acid, the solution warmed gently, which can be done without noteworthy loss, cooled, and made exactly neutral to phenolphthalein: 25 c.c. of glycerol are then added and the titration made. Addition of alcohol renders the end sharper. With mixtures of 100 grams of flesh, and 0.1 gram of boric acid, the results varied from about -5.4 to +1.67 per cent. of the boric acid used.

It has been stated that in cooking salt meat containing boric acid, the greater part of that substance is lost. American salt meat containing 1.12 and 1.17 per cent. of boric acid lost only 0.41 per cent. by soaking and washing, and 0.59—0.67 by boiling; the broth contained 0.60—0.57 part per 100 parts of the original meat. The broth ought therefore never to be consumed.

The authors are experimenting on the use of acetone for separating boric acid and borax. M. J. S.

Estimation of Silicon in Ferro-chromium and of Silica in Chrome Ore. By GEORGE TATE (*Chem. News*, 1899, 80, 235).—Ferro-chromium or chrome ore (1—2 grams) is fused with about five times its weight of sodium peroxide in a nickel crucible, and when cold immersed in water in a nickel dish, neutralised with hydrochloric acid, and evaporated to dryness. The residue is heated with 40 c.c. of strong sulphuric acid until fumes of sulphuric acid appear. When cool, it is treated cautiously with water, transferred to a porcelain dish, made up to about a $\frac{1}{4}$ -litre, boiled to dissolve the sulphates, and the residual silica is washed, dried, ignited, and weighed; if coloured, it is evaporated with hydrofluoric acid and a drop of sulphuric acid, and any residue weighed and deducted. D. A. L.

Estimation of Graphite by Loss. By GEORGE AUCHY (*J. Amer. Chem. Soc.*, 1900, 22, 47—48).—Asbestos is preferable to filter paper for collecting the graphite left on dissolving iron, but attention is called to the retention of water by asbestos (this vol., ii, 309).

The process is not altogether free from sources of error, but these do not appreciably affect the result when the percentage of graphite

is small. The graphite is not always pure carbon, but may contain small quantities of hydrogen, oxygen, nitrogen, and sulphur.

L. DE K.

Iodometric Estimation of Small Quantities of Carbon Monoxide. By LEONARD P. KINNICUT and GEORGE R. SANFORD (*J. Amer. Chem. Soc.*, 1900, 22, 14—18).—The process has been devised for the estimation of small quantities of carbon monoxide in air contaminated by leakage of water-gas, &c. 1000 c.c. of air are drawn through two U-tubes respectively containing sulphuric acid and potassium hydroxide, to absorb unsaturated hydrocarbons, hydrogen sulphide, sulphur dioxide, and similar reducing gases; it then passes through another U-tube containing 25 grams of pure iodine pentoxide, and suspended in an oil-bath heated at 150°. The action of carbon monoxide on the hot iodine pentoxide causes liberation and volatilisation of free iodine, which is collected in a Wolff's blood-absorption-tube containing 0.5 gram of potassium iodide dissolved in 5 c.c. of water. The iodine is then titrated with *N*/1000 sodium thiosulphate.

One milligram of iodine represents 0.4357 c.c. of carbon monoxide.

L. DE K.

Rapid Method of Estimating Carbon Dioxide in Gaseous Mixtures. By LÉO VIGNON and LOUIS MEUNIER (*Compt. rend.*, 1900, 130, 513—515).—A large, cylindrical glass vessel of known capacity is connected with a burette and an inlet tube for the introduction of a gaseous mixture. When the apparatus is filled with the gas, about 40 c.c. of alcohol (93 per cent.), containing a small quantity of phenolphthalein, are run in, and the mixture is titrated with *N*/20 calcium hydroxide solution. The method is applicable to the estimation of carbon dioxide in any mixture of neutral gases; when ammonia and hydrogen sulphide are present, these are removed by passing the gas through an acetic acid solution of lead acetate before collecting it in the titrating cylinder.

G. T. M.

Volumetric Estimation of Magnesia. By JAMES O. HANDY (*J. Amer. Chem. Soc.*, 1900, 22, 31—39).—This is a modification of Stolba's process (1866), which has not found much favour.

The magnesia solution, freed from calcium, aluminium, &c., is precipitated as usual with solution of sodium ammonium hydrogen phosphate, and the precipitate carefully washed with dilute ammonia (1 : 9). When drained, the filter is opened flat and placed on thick, dry filter paper for a few minutes, then transferred to a second dry paper, and left for 30 to 60 minutes, after the moisture has been practically absorbed. The small amount of ammonia still adhering to the precipitate is then expelled by heating for 20 minutes in an air-bath at 50—60°.

The filter with the precipitate is now put into a small beaker, and an excess of *N*/10 sulphuric acid is added. When the precipitate has dissolved and the paper been disintegrated by stirring, two drops of a 0.1 per cent. alcoholic solution of methyl-orange are added, and the excess of acid titrated with *N*/10 sodium hydroxide. 1 c.c. of *N*/10 sulphuric acid = 0.002 gram of magnesia.

L. DE K.

Estimation of Copper. By M. WILLENZ (*Chem. Centr.*, 1900, i, 490; from *Ann. chim. anal. appl.*, 5, 2).—The method of precipitation by sodium thiosulphate is strongly recommended. The substance is dissolved in nitric acid, the solution evaporated with sulphuric acid, and precipitated boiling with 5–6 grams of thiosulphate for each gram of substance. Cadmium and lead are not precipitated, neither are arsenic and antimony if the solution is strongly acid and hot; they separate, however, on cooling and diluting. Traces of both are therefore contained in the copper precipitate, but can be driven off by intense ignition. M. J. S.

Precipitation and Separation of Copper in the Presence of Sodium Hydroxide by the Aid of Hydrazine Sulphate or Hydrochloride. By PAUL JANNASCH and K. BIEDERMANN (*Ber.*, 1900, 33, 631–636).—When a 3 per cent. solution of hydrazine sulphate is added to a copper sulphate solution in the presence of an excess of pure sodium hydroxide and the whole warmed on a sand-bath, the copper is deposited in the metallic state and may be filtered by the aid of a double paper, well washed, dried at 90°, and weighed as cupric oxide after ignition, if necessary, in a current of oxygen.

Copper may be readily separated from zinc or arsenic by this method, as in strongly alkaline liquids only the copper salt is reduced; the zinc may then be precipitated as carbonate and the arsenic as magnesium ammonium arsenate. In the separation of tin and copper, the alloy (1 part) is dissolved in as small a quantity of aqua regia as possible; the solution thus obtained is diluted with its own volume of water and is slowly added to a solution of pure sodium hydroxide (15 parts) and hydrazine hydrochloride (2–3 parts); when the sulphate is employed, small amounts of tin are always carried down with the copper. After the mixture has been warmed for some time, the copper is removed and treated as before; the alkaline filtrate is acidified with hydrochloric acid, precipitated with ammonia, the precipitate dissolved in ammonium sulphide, and reprecipitated as sulphide of arsenic by the careful addition of hydrochloric acid.

J. J. S.

Rapid Estimation of the Purity of Commercial Copper Sulphate, and of the Amount of Copper Sulphate in Copper Pyrites. By CARLO MONTANARI (*Chem. Centr.*, 1900, i, 66; from *Staz. sper. agrar. ital.*, 32, 479).—Zecchini's method (*Staz. sper. agrar. ital.*, 32, 117) gives rapid and exact results, especially if a *N*/20 solution be employed instead of that recommended by Zecchini. Scarlata's method (*Mon. Sci.*, [iv], 13, i, 409) is troublesome and inexact. M. J. S.

Estimation of Aluminium. By ALFRED STOCK (*Ber.*, 1900, 33, 548–553).—The greater part of this paper has already been published (this vol., ii, 247). Aluminium hydroxide, obtained by adding a mixture of potassium iodide and iodate to a faintly acid solution of an aluminium salt, and removing the liberated iodine by sodium thiosulphate (*loc. cit.*), has, after drying in the air, the composition $\text{Al}(\text{OH})_3$; after drying over calcium chloride, the composition $2\text{Al}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$, and after drying at

130°, $3\text{Al}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$; this last hydrate, when exposed to the air, absorbs water until its composition is again represented by the formula $\text{Al}(\text{OH})_3$. The individuality of the various hydrates is being investigated.

In presence of a large excess of sulphates, the precipitated hydroxide contains sulphuric acid, which is, however, lost on ignition. This circumstance interferes with the alkalimetric titration of alum solutions, but the error may easily be avoided by adding a slight excess of barium chloride to the solution, and then titrating as usual without filtering. A. H.

Rapid Method for the Estimation of Clay in Soils. By F. POQUILLON (*Bull. Soc. Chim.*, 1900, [iii], 23, 115—116).—In the process described, the mechanical separation of the sand and clay is facilitated by the use of a dilute solution of ammonium chloride instead of pure water, and the number of washings and bulk of liquid employed is diminished. 10 grams of the soil are rubbed up with 25 c.c. of water, and the liquid mixed with 100—120 c.c. of a 0.1 per cent. solution of ammonium chloride and left for 5 minutes. The supernatant liquid is then decanted, and the operation repeated 6—8 times until the washings are clear, when the residual sand is washed, first with dilute hydrochloric acid and then with water, dried, and weighed. The turbid washings are mixed, acidified with hydrochloric acid, left for 2—3 hours, and the precipitated clay is collected on a filter, washed with water, dried, and weighed. N. L.

Estimation of Nickel in Nickel Ores. By A. C. LANGMUIR (*J. Amer. Chem. Soc.*, 1900, 22, 102—106).—This is a slight modification of Sargent's process (this vol., ii, 51), and may be applied to ores. The method is briefly as follows: the ore is oxidised with nitric acid and bromine, mixed with excess of hydrochloric acid, and boiled down to a small bulk. After diluting with water, copper, &c., are removed by means of hydrogen sulphide. The filtrate is boiled, and the ferrous iron oxidised by cautious addition of nitric acid. Slight excess of ammonia is added, and the filtrate which contains the bulk of the nickel is evaporated in a large casserole. The precipitate is dissolved in hydrochloric acid, boiled down to a pasty mass, dissolved in hydrochloric acid of sp. gr. 1.1, and then agitated with two separate portions of ether. This dissolves the ferric chloride, leaving the nickel in the acid layer. Any iron still remaining is precipitated with bromine and ammonia, and freed from the last traces of nickel by redissolving and precipitating a second time. The ammoniacal solution containing the nickel is now also introduced into the casserole, and the whole evaporated until ammonium chloride begins to separate; this is destroyed by adding a large excess of nitric acid and evaporating to dryness. The nitrate is now converted into sulphate by heating with strong sulphuric acid, the liquid diluted, mixed with excess of ammonia, and submitted to electrolysis. L. DE K.

Rapid Evaluation of Metallic Tungsten Powders. By FRED IBBOTSON and HARRY BREARLEY (*Chem. News*, 1899, 80, 294—295).—Three grams of the powder are ignited in a tared platinum dish until

completely oxidised, re-weighed, treated with hydrofluoric acid to remove silica, and again weighed. It is boiled with pure caustic soda to dissolve as much tungsten as possible, and the residue, which contains iron, manganese, and some tungsten, is collected, washed, ignited, and weighed; it is then dissolved in a small quantity of hydrochloric acid, and should leave no residue if properly ignited at the commencement. The solution is largely diluted to precipitate the tungsten, which is collected and weighed, whilst the iron and manganese may be estimated in the filtrate. The tungsten in the caustic soda solution may also be determined. In this way, with the pure materials used in steel manufacture, useful numbers may be obtained for the silica, tungsten, iron, and manganese. The proportion of tungstic oxide may be ascertained by treating the unheated sample with a large volume of strong hydrochloric acid, which dissolves the oxide, but not the metal. Carbon may be determined by simply heating in a current of oxygen. Sulphur is not usual in samples for steel making, but if present would interfere with the scheme of analysis set forth, and so must be removed beforehand.

D. A. L.

Analysis of Tungsten Compounds. By FRED IBBOTSON and HARRY BREARLEY (*Chem. News*, 1899, 80, 293—294).—On adding strong nitric acid, drop by drop, to a boiling solution of lead tungstate, a change of colour from white to yellow ultimately takes place, boiling for a short time with a few additional c.c. of the acid then develops the full yellow colour of tungstic oxide; the change is quantitative, and may be applied to the estimation of tungsten, making a correction for the small amount of tungstic acid that passes away in the filtrates. Ammonia, if present, is not eliminated; barium, strontium, calcium, magnesium, zinc, cadmium, manganese, nickel, and cobalt do not interfere with the reaction, but arsenic, mercury, uranium, iron, tin, and silicon do, although the interference of arsenic and mercury may be disregarded. In the presence of uranium salts, the solution containing a small excess of sodium carbonate is heated to boiling, and is poured in a thin stream into hot acetic acid containing excess of lead acetate, with vigorous shaking. The mixture is just boiled, the precipitate washed by decantation, &c. The tungstic oxide finally obtained is free from uranium. Iron and aluminium in small quantities may be dealt with by making the solution just alkaline, then faintly acid with acetic acid; most of the tungsten is precipitated with the iron, and the rest is precipitated by lead acetate. The precipitate is washed by decantation, ignited, and treated with hydrochloric acid as though it were pure lead tungstate. Chromium cannot be treated in this manner, and the interference of tin and silicon cannot be avoided. In the last instance, however, the whole of the tungsten may be precipitated from a neutral solution as mercurous silicotungstate by means of mercurous nitrate, the silica in the ignited residue being removed by hydrofluoric acid. Ammonia and ammonium carbonate effect the separation of silica and tungstic oxide imperfectly.

D. A. L.

Ammonium Molybdate as a Delicate Reagent for Stannous Chloride. By J. P. LONGSTAFF (*Chem. News*, 1899, 80, 282—283).—Tin may be detected in solution, in quantities that might escape detection by the ordinary qualitative tests, by means of the blue coloration produced by ammonium molybdate with stannous chloride. The solution, to be tested, must be freshly prepared, and diluted with boiled water to avoid oxidation as much as possible; moreover, it must not contain strong hydrochloric acid, as this destroys the colour. One part of tin, as stannous chloride, in 1,500,000 of solution has been detected by this means. D. A. L.

Significance of the Detection of Nitrites in Drinking Water. By LEOPOLD SPIEGEL (*Ber.*, 1900, 33, 639—644).—The author criticises Erdmann's proposition (this vol., ii, 243) to employ 1-amino-8-naphthol 4:6-disulphonic acid along with sulphanilic acid as a test for nitrites in drinking water. Erdmann's statements that nitrous acid is present in all water containing a small quantity of animal matter, and that every good drinking water is free from nitrous acid, are shown to be erroneous. The author is of opinion that the presence of nitrites in water is no criterion of its value for drinking purposes, as this can only be deduced from a complete examination of the water, coupled with the knowledge of the nature of the soil in which it occurs.

In place of Erdmann's reagent for nitrous acid, the author proposes to use either of the less sensitive compounds, guaiacol and creosote, which, in dilute aqueous solution, give with nitrous acid an orange and a yellow coloration respectively. These reactions are not interfered with by the presence of oxidising agents, such as nitrates, chlorates, and hydrogen peroxide, or by ferric salts in such concentrations as are met with in potable waters. T. H. P.

Cobalticyanides. By EDMUND H. MILLER and JOHN A. MATHEWS (*J. Amer. Chem. Soc.*, 1900, 22, 62—69).—The authors give instructions for the preparation of the metallic cobalticyanides, and their chief properties are described in an accompanying table.

Potassium cobalticyanide may perhaps be used in quantitative analysis. As the lead salt is very soluble, whilst those of silver, copper, and bismuth are insoluble in water or nitric acid, it may perhaps be useful in the assay of pig lead. The bismuth may then be separated from the copper by treatment with hydrochloric acid, which dissolves the bismuth cobalticyanide and leaves the copper, together with any silver compound, undissolved; or by treating the precipitate with ammonia in which the copper and silver compounds dissolve, leaving the bismuth. The bismuth may be separated from the compound as hydroxide by digesting it with aqueous potassium hydroxide.

It also affords a means of separating zinc, manganese, nickel, or cobalt from ferric iron, as the latter is not precipitated in the presence of sufficient ammonium sulphate. The zinc compound may be separated from the others by dissolving it in aqueous potassium hydroxide, which leaves the manganese, cobalt, and nickel in the form of hydroxides. Further results are promised. L. DE K.

Chemistry and Analysis of Wines. By MAXIMILIAN RIPPER (*Chem. Centr.*, 1900, i, 436—437; *Zeit. Landw. Vers.-Wesens. Oesterr.*, 3, 26).—In continuation of previous work on this subject (*Abstr.*, 1899, ii, 699), attention is directed to the aldehydes and their compounds contained in wine. Aldehydes or ketones may be detected in all wines by distilling 200 c.c. of the wine, and testing the first 20 c.c. of the distillate with phenylhydrazine hydrochloride, Guyon's reagent, *m*-phenylenediamine hydrochloride, ammoniacal silver solution, or resorcinol and hydrochloric acid. For estimation, 50 c.c. of the wine are mixed with 5 c.c. of sulphuric acid (1 : 3) and some starch, and titrated with *N*/50 iodine solution. To another 50 c.c. in a flask 50 c.c. of *N*/50 potassium hydrogen sulphite are added, and the corked flask is kept for $\frac{1}{4}$ hour, at the end of which time 5 c.c. of sulphuric acid are added and the mixture is titrated with the iodine solution. The iodine value of the sulphite solution is also estimated. The amount of iodine required by the wine alone is subtracted from that consumed by the mixture of wine and sulphite, and this difference is subtracted from the amount of iodine required by the sulphite alone. The difference is calculated into acetaldehyde. M. J. S.

Estimation of Cresols by Determining their Capability of forming Bromo-substitution Derivatives. By ROBERT CLAUSER (*Chem. Centr.*, 1900, i, 118; from *Oesterr. Chem.-Zeit.*, 2, 585—588).—*o*-Cresol may be estimated by Koppeschaar's method, with a maximum error of +0.5 per cent. The solution should contain only 1/30,000—1/40,000th of its weight and the quantity of the bromide-bromate solution added should be sufficient to supply 6 atoms of bromine for each mol. of cresol present. As soon as the yellow coloration appears, the action requires to be checked by adding potassium iodide and allowing the mixture to remain for half an hour.

E. W. W.

Estimation of the Reducing Power of Urine, Blood, and other Animal Fluids. By HEINRICH ROSIN (*Chem. Centr.*, 1900, i, 48; from *Münch. med. Woch.*, 46, 1456).—The author formerly proposed to effect this object by ascertaining the amount of methylene-blue decolorised by a given volume of the urine under certain conditions. A more satisfactory method is to use the methylene-blue merely as an indicator, and to employ potassium permanganate as the oxidising agent. The urine is diluted five-fold; 25 c.c. are placed in a small Erlenmeyer flask, mixed with 1 c.c. of officinal potassium hydroxide solution, covered with paraffin oil to exclude air, and heated, but not to boiling. From a burette, the point of which dips below the paraffin layer, 1 c.c. of methylene-blue solution (1 : 3000) is then introduced, and then in a similar manner *N*/100 permanganate, until a bluish-green colour is obtained. The permanganate required is a measure of the reducing power of the urine. M. J. S.

Detection of Sucrose in Margarine. By MECKE (*Chem. Centr.*, 1900, i, 435; from *Zeit. öffent. Chem.*, 5, 496).—To communicate to margarine the properties of natural butter, sucrose and yolk of egg are added to it. Sucrose can be estimated in presence of lactose by the polarimeter, but the difficulty of obtaining clear solutions from

margarine renders this method inadmissible. The sugars are therefore estimated gravimetrically before and after inversion with citric acid.

M. J. S.

Analysis of Golden Syrup. By RICHARD BODMER, NORMAN LEONARD, and HARRY M. SMITH (*Analyst*, 1899, 24, 253—257).—Attention is called to the growing practice of adulterating golden syrup with glucose, the product of the hydrolysis of starch.

The adulteration may be detected and even approximately estimated by taking the copper-reducing power of the sample (calculated on the dry substance) before and after inversion; another inversion experiment is made in which not only the sucrose but any dextrin or maltose is also inverted. The copper-reducing power, coupled with a polarimetric test, is sufficient to enable an opinion to be formed on the sample. In the equation given to facilitate the calculation, it is assumed that commercial starch-glucose has a copper-reducing power of 53 and a specific rotation of $+134^\circ$ for sodium light. The analyses of several commercial samples of golden syrup are given in a table (compare following abstract).

L. DE K.

Analysis of some Sugar Syrups. By ALEXANDER K. MILLER and J. P. PORTS (*J. Soc. Chem. Ind.*, 1899, 18, 1091—1093).—The authors criticise the process recently introduced by Bodmer, Leonard, and Smith (preceding abstract).

Owing to the uncertain nature of commercial glucose, analyses made by means of the polariscope are untrustworthy quantitatively, although they have a qualitative value. For such a qualitative test, the following procedure is recommended:—Determine the polarimetric reading of a 10 per cent. solution (or other suitable strength) of the syrup; invert the cane-sugar in a portion of the solution and again determine the rotation. From the difference between the two readings, the cane-sugar can be determined, and from this the rotation due to the cane-sugar calculated. If this is deducted from the original rotation, the difference will represent the rotation due to the dextrose and lævulose, if the sugar is a genuine sugar syrup, and the result will generally be a lævo-rotation. The process should be supplemented by a fermentation experiment; further investigation seems very desirable.

L. DE K.

Effect of the Presence of Glycuronic Acid on the Phenylhydrazine Test for Sugar in Urine. By PAUL MAYER (*Chem. Centr.*, 1900, i, 284—285; from *Berlin klin. Woch.*, 37, 5—7. Compare this vol., ii, 155).—When ordinary urine is treated with phenylhydrazine and a 50 per cent. solution of acetic acid, a brown, amorphous precipitate is formed which consists chiefly of a decomposition product of phenylhydrazine, probably diphenylhydrazine. When, however, the urine contains large quantities of derivatives of glycuronic acid, a phenylhydrazine compound may be obtained, as some of these glycuronic acid compounds are decomposed by heating with acetic acid. Thus, whilst urines containing thymol- or naphthol-glycuronic acid do not give phenylhydrazine compounds, a crystalline substance melting at $200\text{--}215^\circ$ may be obtained from a urine containing mentholglycuronic acid, but in this case, although the urine

slowly reduces Fehling's solution and is slightly lævorotatory, it cannot be fermented. The decomposition of mentholglycuronic acid also takes place when the urine is kept, orcinol and menthol being formed. Urines containing urochloralic acid and more than normal amounts of phenol-, indoxyl-, or scatoxyl-glycuronic acid also yield phenylhydrazine compounds. In all these cases, however, the fermentation test furnishes a trustworthy indication of the presence or absence of sugar.

E. W. W.

Isolation of Glycogen from Horseflesh and Preserved Meats. By G. BREUSTEDT (*Arch. Pharm.*, 1899, 237, 637—659).—Several methods of isolation have been studied, and the properties of the glycogen compared with those of the products formed at the same time from any pepper present in the sausages, &c. The conclusion is drawn that at present it is impossible to isolate glycogen with certainty from sausages containing pepper as well as horseflesh; in any case, the employment of alkalis should be avoided when pepper is present, and water used for the extraction. For all preparations that contain no starch, the use of alcoholic, rather than aqueous, potash is recommended in order to extract the glycogen.

The method is as follows: The meat is minced finely and freed from fat by kneading it with warm light petroleum, and decanting the latter; 100 grams of it are mixed in a beaker with 25 c.c. water, 100 c.c. of 90 per cent. alcohol, and 7 grams of caustic potash if the meat is fresh, or 10—15 grams if it has been smoked and more or less dried. The whole is then warmed on the water-bath and stirred for 20—60 minutes, until the muscle fibres are destroyed. The now fairly thin liquid is diluted to 350 c.c. with 95 per cent. alcohol, and allowed to remain at 40° until the solid matter has settled; the liquid is decanted through a plug of glass wool, and the residue washed twice with 50—75 c.c. of alcohol (60 per cent. by vol.). The glass wool is now placed in the beaker, the alcohol remaining evaporated off, the residue mixed with 25 c.c. of water, acidified with hydrochloric acid, and treated with Brücke's reagent (*Sitzungsber. Wien. Akad.*, 1871, Abt. II., Bd. 63) until a further addition of this produced no precipitate. The precipitate is collected and washed with a little water containing a few drops of hydrochloric acid and Brücke's reagent, the filtrate precipitated with twice its volume of 95 per cent. alcohol, and filtered after a little while. The filter is then perforated, the precipitate rinsed with a little hot water into a beaker, the liquid acidified with hydrochloric acid when cold, and treated with a few drops of potassium mercuriodide solution, to precipitate any proteids still present, filtered, the precipitate washed as before, the filtrate mixed with twice its volume of alcohol, and the precipitate of glycogen collected at once on a filter (previously dried at 110° and weighed), washed first with 95 per cent. alcohol, and then with ether, dried at 110°, and weighed.

C. F. B.

Estimation of Glycogen, and Relative Quantities of Glycogen in Different Parts of the Flesh of the Horse. By JOHN K. HAYWOOD (*J. Amer. Chem. Soc.*, 1900, 22, 85—93).—50—60 grams of ground meat are heated with 300 c.c. of a 1 per cent. solution of potassium

hydroxide for 6 hours on the water-bath, water being added from time to time so as to keep the volume of the liquid at 150 c.c. Dilute hydrochloric acid (1 : 5) is now added until the liquid is slightly acid and solution of mercuric potassium iodide (a 10 per cent. solution of potassium iodide saturated with mercuric iodide at boiling heat) is added so long as a precipitate is formed. The whole is diluted to 500 c.c., well shaken, and 250 c.c. collected by filtering through a fluted filter. After adding a drop or two of phenolphthalein, the liquid is neutralised with potassium hydroxide, the amount used being noticed; if a precipitate forms, the liquid must be again filtered and an aliquot part of the filtrate collected, 3—4 drops of hydrochloric acid added, and then twice the volume of 95 per cent. alcohol. After a few hours, the glycogen is collected on a filter, washed first with 60 per cent., then with 95 per cent. alcohol, and finally with ether. The filter is dried at 105° and weighed; the glycogen is now extracted with boiling water and after drying at 115°, the filter is reweighed. Tables are given showing the amount of glycogen in the various parts of the carcase of the horse.

L. DE K.

New Method for the Estimation of Acetic Acid in Vinegar. By DURIU (*J. Pharm.*, 1900, [vi], 11, 22—23).—As the ordinary methods for the estimation of acetic acid in vinegar are not applicable when the liquid is highly coloured, the following method has been devised. 6 c.c. of a solution of sodium hydrogen carbonate (1/20) are introduced into a graduated tube, then 6 c.c. of alcohol (95°) are carefully added, care being taken that the liquids do not mix. 1 c.c. of a 7 per cent. solution of acetic acid is next added, the tube closed with the thumb, shaken and inverted over water, and the volume of gas evolved is noted. A similar experiment is made with the vinegar, and from the volume of gas evolved and the data obtained in the first experiment, the percentage of acetic acid is readily calculated. It is, of course, essential that the vinegar should contain no other acid than acetic acid.

H. R. LE S.

Estimation of Oxalic Acid in Acid Beet Leaves. By KARL BÜLOW (*Chem. Centr.*, 1900, i, 374; from *J. Landw.*, 47, 359—367).—This is a slight modification of Schloësing's process. 5 grams of the leaves are rubbed in a mortar with 5 c.c. of 22 per cent. sulphuric acid and 5—6 grams of pumice powder added so as to form a dry mass. The mixture is then placed in an open glass tube plugged at the lower end with cotton wool and extracted with ether. The ethereal solution is put into a beaker containing 50 c.c. of water and heated on the top of a water-oven until the ether has evaporated. The aqueous liquid is filtered, neutralised with ammonia, again acidified with acetic acid, and precipitated with calcium acetate; the precipitated calcium oxalate is freed from sulphate by repeated solution in hydrochloric acid and reprecipitation with ammonia.

L. DE K.

Action of Iodine Solution and Alkaline Permanganate on Uric Acid. By ADOLF JOLLES (*Zeit. physiol. Chem.*, 1900, 29, 193—204).—It has been stated by Kreidl (*Abstr.*, 1893, ii, 558)

that in alkaline solution uric acid can be estimated by adding an excess of iodine solution, and after the lapse of $\frac{3}{4}$ hour, acidifying the mixture and titrating the unabsorbed iodine, but that a shorter time results in the consumption of more iodine. The author shows that the anomaly is due to the fact that uric acid slowly decomposes potassium iodide with liberation of iodine. By allowing the action to proceed for exactly $\frac{3}{4}$ hour, the amount of iodine consumed is proportional to that of uric acid present, but with a prolongation of the time the amount increases, although Kreidl's ratio of 3.5 atoms of iodine to 1 mol. of uric acid was not even approximately attained. The method therefore seems useless for practical purposes. Experiments with Hübl's reagent gave a similar result, but potassium iodide being absent the anomaly noticed above does not occur.

The author confirms the accuracy of Hopkins's method of titrating uric acid with permanganate in acid solutions, but experiments on the action of permanganate in alkaline solutions show that the amount reduced depends (1) on the quantity of permanganate added, and (2) on the length of the boiling, and is, moreover, largely increased by the presence of ammonium carbonate, which, according to Folin's method, is employed for washing the ammonium urate precipitated from urine by ammonium acetate. M. J. S.

Hübl's Iodine Method for Oil Analysis. By AUGUSTUS H. GILL and WALTER O. ADAMS (*J. Amer. Chem. Soc.*, 1900, 22, 12—14).—A process is described which is quite as easy of execution as the original Hübl method, and has the advantage of giving the true iodine figure.

30 grams of mercuric iodide and 25 grams of iodine are dissolved in a litre of pure absolute methyl alcohol and 30 c.c. of this solution are then used in the test. The results differ slightly from those of Hübl. The average iodine absorption of pure oleic acid is given as 90.2, that of olive oil as 79, of cotton seed oil as 91.9, of prime lard as 71.8, and of neat's-foot oil as 55.8 per cent. L. DE K.

The Determination of the Iodine Value. By JULIUS LEWKOWITSCH (*Analyst*, 1899, 24, 257—259).—Hübl's process for the iodine value of oils has been modified by Wijs (*Abstr.*, 1898, ii, 412), who recommends using a solution of iodine monochloride in pure glacial acetic acid instead of a solution of iodine and mercuric chloride in alcohol; this solution is infinitely superior to the alcoholic solution as regards stability.

The author now states that both solutions, if carefully applied, give identical results. L. DE K.

The Meaning of the Acetyl Value in Fat Analysis. By JULIUS LEWKOWITSCH (*Analyst*, 1899, 24, 319—330. Compare *Abstr.*, 1898, ii, 316).—The author has ascertained the acetyl number of many fats, waxes, and oils, and has tabulated the results.

The acetyl value indicates the presence of hydroxy-acids, free

alcohols, oxidised fatty acids, and unknown acids, to which must be added mono- or di-glycerides and rancid fats. L. DE K.

Rapidity of Saponification of Some Fats. By HANS KREIS and OTTO WOLF (*Chem. Centr.*, 1900, i, 376; from *Zeit. Unters. Nahr.-Genussm.*, 2, 914—915).—By means of Henriques' cold saponification process, the progress of the reaction being investigated at fixed intervals, it has been proved that there is no appreciable difference in the rate of saponification of butter and margarine. The saponification of beef-tallow proceeds the most quickly. Olive oil, during the first hour, is saponified more slowly, but afterwards more rapidly, than butter. L. DE K.

Analysis of Milk. By L. GALLIEN (*J. Pharm.*, 1900, [vi], 11, 61—64).—In the estimation of lactose in milk by the ordinary polarimetric method, quite an appreciable error is introduced by the fact that the milk serum examined is regarded as occupying the same volume as the original milk, and no account is taken of the volume occupied by the casein, albumin, and butter fat. A simple method of analysis, and a formula and a set of tables are given, by the use of which the true percentage of lactose in milk may be determined.

H. R. LE S.

Modification of Duclaux's Method for Estimating Total Solids and Fat in Milk. By UMBERTO MORINI (*Chem. Centr.*, 1900, i, 69; from *Staz. sper. agrar. ital.*, 32, 517).—Duclaux's method (*Le lait*, 1887, 20, 176), and *Principes de laiterie*, 111, 258) is especially suitable for butters containing much water and proteids. The author prefers, however, to work with 20 grams of substance, and to extract the fat with Förster's apparatus (*Zeit. anal. Chem.*, 1888, 27, 30). M. J. S.

Estimation of Fat in Milk. By R. LÉZE (*Chem. Centr.*, 1900, i, 69; from *Ann. chim. anal. appl.*, 4, 371).—8 grams of caustic potash are dissolved in 10 c.c. of pure ammonia, 55 c.c. of ethyl alcohol, and 15 c.c. of amyl alcohol are added, and the mixture made up to 100 c.c. with ammonia. 36 c.c. of the milk and 10 c.c. of the above mixture are placed in a 50—60 c.c. flask which has a narrow neck graduated in tenths of a c.c., and after heating for 10 minutes in boiling water, the clear fat is driven up into the neck by adding water, and its volume read off at 40°. As milk fat has an average density of 0.9 at 40°, one-fourth of the volume gives grams of fat per litre of milk; the results agree well with those obtained by extraction. M. J. S.

Changes in the Constants of Butter Fat under the Influence of Feeding. By A. RUFFIN (*Chem. Centr.*, 1900, i, 69—70; from *Ann. chim. anal. appl.*, 4, 383).—The author finds numerous analytical anomalies in Baumert and Falke's work (*Abstr.*, 1899, ii, 689). His own observations on the influence of feeding with various kinds of oil-cake on the composition of the butter, originally published in 1890, gave the following numbers:

	Refraction.	Saponification number.	Volatile fatty acids.
Ordinary fodder, hay, lucerne...	30 —33	224 —232	27·6—34·9
Cotton-seed cake	28·5—30	222 —228	26·4—29
The same, with ordinary fodder	29·5—30	221 —229	28·4—30
Earthnut cake	30 —31	225 —228	26·9—29
The same, with ordinary fodder	28 —30	221·9—229	28 —32
Cocoanut oilcake	32 —33	231 —240	25·5—31

M. J. S.

Testing Margarine and Butter for Sesamé Oil. By HERMANN BREMER (*Chem. Centr.*, 1900, i, 374—375; from *Pharm. Zeit.*, 45, 7—8).—A controversy with Soltsien on the value of the furfuraldehyde test for sesamé oil. If the reagents are pure, the process is not likely to cause error.

L. DE K.

Testing Margarine and Butter for Sesamé Oil. By PAUL SOLTSIEN (*Chem. Centr.*, 1900, i, 375; from *Pharm. Zeit.*, 55, 25—26).—A reply to Bremer (preceding abstract). The author states that the colour produced by furfuraldehyde and hydrochloric acid is not always due to sesamé oil.

L. DE K.

Halphen's Reaction and its Application to the Estimation of Cotton-seed Oil. By CASIMIR STRYZYOWSKI (*Chem. Centr.*, 1900, i, 373; from *Pharm. Post*, 32, 736—738).—The author confirms the trustworthiness of Halphen's test; it may be used also for the estimation of cotton-seed oil in other oils. 2 c.c. of the fat and 2 c.c. of the reagent are heated on a boiling water-bath for 45 minutes, the residue is diluted with carbon disulphide to 6 c.c., and the depth of the red coloration compared with that produced by a mixture of known composition under the same conditions. If, however, the added cotton-seed oil has been heated to 200°, the estimation is no longer trustworthy.

The active principle which causes the reaction is not removed from the oil by animal charcoal. If cotton-seed oil is treated with Bechi's reagent until this no longer gives a reaction, and filtered, the filtrate does not give the Halphen test.

L. DE K.

Analysis of Fish Oils [Thranen]. By HENRIK BULL (*Chem. Zeit.*, 1899, 23, 996).—Some kilograms of fatty acids derived from fish oil are distilled in a current of superheated steam at 200°, and then passed through a series of receivers, the temperatures of which are 160°, 140°, 120°, and 100° respectively. Four groups of fatty acids are thus obtained, analytical data of which are communicated.

Four groups of acids may also be obtained as follows. The oil is saponified with solution of potassium hydroxide in absolute alcohol, and the potassium soap crystallised as far as possible. After recovering the fatty acids from the mother liquor, they are treated with alcoholic soda, and further crystals of sodium soap obtained. The mother liquor is now evaporated to dryness, and the residue treated with anhydrous ether, to obtain the sodium salts readily soluble in that solvent; on agitating the ether with water, some remain in solution, whilst others pass into the aqueous layer.

L. DE K.

Analysis of Soap. By AL. A. SHUKOFF and K. T. NOGIN (*Chem. Centr.*, 1899, ii, 1140—1141; from *Chem. Rev. Fett.-Harz-Ind.*, 6, 205—207).—4—5 grams of the sample, taken from the centre by means of a cork borer, are quickly weighed in a beaker and gently warmed with 30 c.c. of normal sulphuric acid until the fatty acids are perfectly liquefied. When cold, the aqueous liquid is filtered, and the fatty acids again melted, and treated with 30 c.c. of water, which is afterwards poured through the same filter. The cake is washed thrice with cold water, and then dissolved in alcohol; the solution is evaporated in a weighed dish, and the residue dried for 20 hours at 95—100°. The molecular weight of the acids is then found by dissolving them in 10 c.c. of alcohol, and titrating with normal sodium hydroxide. The acid filtrate is also titrated, and the loss in sulphuric acid represents the total alkali; the difference between this and the alkali required by the fatty acids represents free alkali.

A direct estimation of the water in soap is not advisable.

L. DE K.

Water-softening (or so-called "scouring") Power of Soaps. By FREDERIC W. RICHARDSON and ADOLF JAFFÉ (*J. Soc. Chem. Ind.*, 1899, 18, 998—1001).—2.5 grams of the soap are dissolved in 40 c.c. of diluted methylated spirit (? proof strength), and this solution is diluted to 250 c.c. The liquid is then added from a burette to 100 c.c. of Clark's standard hardness solution (16 grains of calcium carbonate per gallon) until the lather is permanent for one minute. The authors prefer making the stock solution 10 times the usual strength, and then diluting it before use. An average curd soap gives a reading of 28 c.c.; the foam value or water-softening power of the sample is then expressed by $x = 2800/A$, where A represents the number of c.c. of soap solution required to give the requisite foam. Results are communicated in a table, from which it appears that there is no strict relation between the total fatty acids in soaps and their scouring power.

L. DE K.

Estimation of Formaldehyde. By the VEREIN FÜR CHEMISCHE INDUSTRIE IN MAINZ (*Zeit. anal. Chem.*, 1900, 39, 60—63).—The following procedure is adopted for Romijn's titration by iodine (*Abstr.*, 1897, ii, 166): 30 c.c. of normal sodium hydroxide and 5 c.c. of the dilute formaldehyde solution are placed in a well-stoppered bottle, and $N/5$ iodine (40—70 c.c.) added until the liquid becomes yellow. After shaking for about a minute, the liquid is acidified with 40 c.c. of normal acid, and the residual iodine titrated with $N/10$ thiosulphate. A blank titration should be made.

The estimation by the reaction with an alkali hydroxide, $2\text{HCHO} + \text{NaOH} = \text{HCO}_2\text{Na} + \text{MeOH}$, is recommended in the following form: 50 c.c. of normal sodium hydroxide are placed in a strong, narrow-necked 250 c.c. flask and 5 c.c. of the formaldehyde solution, added. The flask is closed with a rubber stopper and completely immersed in water which is kept for 7 hours at 85—87°; after cooling, the excess of alkali is titrated. Several estimations should be made simultaneously, and only those accepted in which the mixture remains colourless; a yellow coloration would indicate secondary reactions.

The same reaction may be employed for estimating methyl alcohol in formalin, 100 grams of which are cohobated for 2 hours with 700 grams of 2*N* sodium hydroxide, using a condenser cooled by ice to avoid loss of methyl alcohol. The methyl alcohol is then distilled off and its amount ascertained from the density of the distillate. From the total quantity found, that resulting from the formaldehyde present is then deducted. The results are of only approximate accuracy, since secondary reactions cannot be wholly avoided.

Another method depends on oxidation with a standard potassium dichromate solution acidified with sulphuric acid. The mixture (0.5 gram of formaldehyde, 2.952 grams of dichromate, 3.2 grams of sulphuric acid, and 100 c.c. of water) is heated in a sealed tube for 6 hours at 140°, and the unreduced chromate then estimated with potassium iodide and thiosulphate. The methyl alcohol, formaldehyde and formic acid present are all oxidised to carbon dioxide and water, and after deducting the amount of chromate reduced by the two latter, the remainder is calculated into methyl alcohol.

M. J. S.

Estimation of Chloral Alcoholate. By FRANZ SCHMIDINGER (*Monatsh.*, 1900, 21, 36—38).—The author shows that Zeisel's method of estimating ethoxy-groups by treatment with hydrogen iodide, and determining the ethyl iodide formed, will also serve to determine the amount of alcoholate present in impure specimens of chloral hydrate.

R. H. P.

[Detection of] Furfuraldehyde in Beer. By C. HEIM (*Biedl Centr.*, 1900, 29, 71; from *Zeit. ges. Brauwesen*, 21, 155—158).—Test paper for furfuraldehyde is prepared by soaking thick filter-paper in a solution of freshly-distilled aniline (9 parts) in glacial acetic acid (6 parts). The solution must be protected from air and light, and must be frequently renewed. By means of this paper, 1 part of furfuraldehyde can be detected in 1,000,000 parts of beer; 1 part in 100,000 is sufficient to affect the taste of beer.

Whilst furfuraldehyde could be detected in English and Belgian beer, Munich beer was found to be free from it. The process of brewing employed in Munich renders the production of furfuraldehyde impossible. The greater the amount of acid in beer, the more readily is furfuraldehyde detected.

N. H. J. M.

Estimation of Vanillin. By PAUL WELMANS (*Zeit. anal. Chem.*, 1900, 39, 58—60; from *Pharm. Zeit.*, 1898, 634).—A gram of the substance is dissolved in 25 c.c. of alcohol and shaken in a stoppered bottle with 25 c.c. of *N*/2 alcoholic potash until completely dissolved. The excess of potash is then titrated with *N*/2 hydrochloric acid and phenolphthalein. The exact value of the 25 c.c. of potash is estimated under similar conditions, and the difference, multiplied by 0.076, gives the amount of vanillin. Of vanillin sugar, 10 grams are dissolved in 50 c.c. of water, the alcoholic potash is added, and the operation carried on as above. The presence of vanillic acid confuses the end-point. To detect acetanilide, an adulterant frequently employed, 1 gram of vanillin, may be dissolved in 10 c.c. of normal potash; acetanilide remains undissolved unless heat is applied.

M. J. S.

Estimation of Glycyrrhizin in Liquorice Extract. By B. HAFNER (*Chem. Centr.*, 1900, i, 68; from *Zeit. Oesterr. Apoth. V.*, 37, 542).—Ten grams of the coarsely powdered extract are warmed for several hours with 200 c.c. of 95 per cent. alcohol and 25 c.c. of *N* sulphuric acid, and the insoluble matter is washed with alcohol. The filtrate, made feebly alkaline with ammonia, and diluted with an equal volume of water, is evaporated, made up to 100 c.c. with water and a few drops of ammonia, filtered, and precipitated with dilute sulphuric acid. The precipitated glycyrrhizin is washed with 2—3 per cent. sulphuric acid, dried in the desiccator, and then extracted with acetone on the water-bath. After adding water and barium carbonate, the acetone is expelled on the water-bath, the residue digested with 200 c.c. of hot water, and the filtered solution evaporated, dried at 100°, and weighed. The barium glycyrrhizate thus obtained should contain 18.76 per cent. of barium, which may be confirmed by evaporating with sulphuric acid, and igniting. M. J. S.

The Florence Reaction. By HEINRICH STRUVE (*Zeit. anal. Chem.*, 1900, 39, 1—8).—The iodine reaction proposed in 1895 by Florence for the medico-legal detection of stains produced by spermatic fluid has no special character, but is produced by all substances of the choline group, such as betaine, neurine, muscarine, amanitine, sinalbin, sinigrin, &c. The mode of using the reagent must be varied somewhat according to the substance under examination, but the general method is as follows. A few drops of an aqueous solution or extract of the substance are dried at 100° on an object glass, then moistened with a solution containing 6 parts of potassium iodide and 2 parts of iodine in 100 parts of water, and, after the superposition of a cover-glass, observed with a magnifying power of 70. After a few moments, peculiar, brownish-black crystals are seen. Should no result be obtained, the experiment is repeated with addition of some dilute hydrochloric acid. In other cases, special methods are necessary for obtaining the reaction. The reaction has been observed with nasal mucus, phlegm, blood, ethereal extract of yolk of egg evaporated with hydrochloric acid for the decomposition of the lecithin, and with many substances of vegetable origin, such as extracts of black and white pepper, *Penicillium glaucum*, *Secale cornutum*, extracts of leaves, flowers, and fruits, and even with wine. From coffee berries, and the leaves of *Erythroxylon coca*, however, no crystals could be obtained. Nothing is known as to the composition of the brown crystals, as their existence is extremely ephemeral. Their growth can be followed under the microscope, but as soon as they reach a maximum size they begin to liquefy and disappear. They can be reproduced as often as desired by redrying the preparation and treating afresh with the reagent. These facts indicate the great stability and wide distribution of substances of the choline group. M. J. S.

General and Physical Chemistry.

Chemical Action of Light contrasted with that of the Silent Electric Discharge. By MARCELLIN P. E. BERTHELOT (*Ann. Chim. Phys.*, 1900, [vii], 19, 150—154. Compare Abstr., 1897, i, 330; 1898, ii, 393; 1899, i, 657; ii, 1, 197; and this vol., i, 3).—Benzene remains unaltered when exposed to bright sunlight for several months in sealed tubes containing hydrogen or argon, although it combines with oxygen, yielding resinous products; if placed over mercury, a brown sediment, which is derived from the thiophen present in the hydrocarbon, forms at the junction of the liquids. Carbon disulphide, under these conditions, undergoes a partial decomposition, and the sides of the containing vessel become coated with a brown deposit; when exposed to diffused light, it remains unaltered, and does not react with hydrogen or argon.

When a mixture of argon and gaseous carbon disulphide is submitted to the action of the silent electric discharge for three months in diffused light, the electrodes being maintained at a difference of potential of 200 volts, the former gas remains unaltered, whilst 60 per cent. of the latter is converted into yellow, resinous products. G. T. M.

Influence of Pressure on the Rotation of Solutions of Sucrose. By L. H. SIERTSEMA (*Arch. néerland sci. exp. nat.*, 1899, [ii], 3, 79—87).—The rotations of solutions of sucrose at various pressures were determined, plates of quartz being used to partially compensate the rotation of the solution and render small variations more evident. The variation of rotation for 100 atmospheres pressure are then calculated, and corrections introduced for the variation of rotation of the quartz, after which the variation of rotation per centimetre is calculated. This is dependent on the variation of concentration and of specific rotation, and, of these, the first is calculable from Amagat's compressibility values. The values so obtained are as follows, where c is concentration, k the internal pressure according to Tammann, $\Delta c/c$ the concentration change, $\Delta \beta/\beta$ the change of rotation per cm., and $\Delta \gamma/\gamma$ the change of specific rotation = $\Delta \beta/\beta - \Delta c/c$.

c .	k .	$\Delta c/c$.	$\Delta \beta/\beta$.	$\Delta \gamma/\gamma$.
9.48	238	0.00449	0.00268	—0.00181
18.70	465	0.00418	0.00252	—0.00166
27.84	669	0.00398	0.00270	—0.00128

If, as Tammann supposes, the variations of specific rotation with concentration are due to variations of internal pressure, then, by the use of the above values for $\Delta \gamma/\gamma$, the internal pressure of the solutions is calculable, but the values do not agree with those obtained by Tammann by other methods; the author, however, makes no attempt to estimate the undoubtedly great probable error in the above values of $\Delta \gamma/\gamma$. In many cases, the variations of rotation consequent on the addition of an inactive salt are completely explicable on Tammann's hypothesis, but, as agreement is not found in all cases, the author

considers that Tammann's theory is insufficient to explain the changes of rotation (compare Tammann, *Abstr.*, 1896, ii, 13, 289, and previous abstracts).

L. M. J.

Spectrum of Bromine. By JOSEF M. EDER and EDUARD VALENTA (*Chem. Centr.*, 1900, i, 453; from *Denkschr. math.-nat. Klasse K. Akad. Wiss. Wien.*, 1—8).—The line spectrum is most distinct with a pressure of 8—10 mm.; when the pressure is lowered, the spectrum becomes faint, and when the pressure is raised, there is marked broadening of the lines. Besides this line spectrum, a continuous spectrum was observed in the violet also at low pressures. A third spectrum was observed at a pressure of 45 mm., corresponding probably with the normal band spectrum of other elements. The authors consider the line spectrum especially characteristic.

J. C. P.

Fluorescence of Metallic Compounds under the Influence of Röntgen and Becquerel Rays. By PAUL BARY (*Compt. rend.*, 1900, 130, 776—778).—The author has examined a large number of salts under the influence of the Röntgen rays; those which become fluorescent belong, with the exception of uranium, to the families of the alkalis and alkaline earths; of these salts, the halogen compounds appear to always become fluorescent, but many other salts may be inactive. Similar results were obtained by exposure to the radiations from a radio-active metal supplied by Curie (compare this vol., ii, 82, 126), and these are also probably radiations of very short wave-length. The permanent luminescence of some barium salts may be due to the action of the Becquerel rays on the barium salt itself, or to the fluorescence of contained radium.

L. M. J.

Nature of Electrocapillary Phenomena. I. Their Relation to the Potential Differences between Solutions. By S. W. J. SMITH (*Phil. Trans.*, 1899, A, 193, 47—87; also *Zeit. physikal. Chem.*, 1900, 32, 433—476).—The Lippmann-Helmholtz theory of the capillary electrometer contains two assumptions. According to the first, the variation of the potential difference at the capillary electrode of an electrometer is the same as that of the applied E.M.F. To test this, the effect of depolarisation has been investigated and determined. The second assumption, that electrocapillary phenomena depend simply on the variation of the electrostatic surface energy, leads to difficulties, for (1) the form of the electrocapillary curve is remarkably dependent on the nature and concentration of the electrolyte; (2) if it be assumed that the potential difference between the solution and the capillary electrode is zero when the surface tension is a maximum, large potential differences must exist between certain solutions.

According to the Nernst-Planck theory, the potential difference between equally concentrated solutions of potassium chloride and potassium iodide is negligible; with this conclusion, the first assumption of the Lippmann-Helmholtz theory is in accord. Combination of the two hypotheses shows that the surface tension of mercury (for a certain range of potential differences) in two solutions is the same for a given potential difference between the mercury and the respective solutions, if they are equally concentrated and possess the same

cation; it is further shown that it is immaterial whether the cation be K, Na, or H.

The work described in the paper points to the first assumption of the Lippmann-Helmholtz theory being correct, and the second incorrect; the electrocapillary curves are never completely free from influences other than electrostatic. J. C. P.

Potential Differences with Manganese Dioxide Electrodes. By OLIN F. TOWER (*Zeit. physikal. Chem.*, 1900, 32, 566—577).—Experiments are recorded supplementing the author's previous work (Abstr., 1896, ii, 142) and that of Smith (Abstr., 1897, ii, 5). The concentration of the H^+ ions in a solution at a manganese dioxide electrode is found to have about four times as much influence on the E.M.F. as the concentration of the Mn^{++} ions. A number of experiments have been made to determine by this method the dissociation of numerous dibasic organic acids, but the author concludes that the method is not exact. The differences between the results actually obtained and those theoretically deducted cannot be satisfactorily explained. J. C. P.

Dielectric Constant of Hydrogen Peroxide. By HARRY T. CALVERT (*Ann. Phys.*, 1900, [iv], 1, 483—485).—The dielectric constant of a 45.9 per cent. solution of hydrogen peroxide, as determined by one of Drude's methods (Abstr., 1897, ii, 438), has the value 84.7 at 18°. If the density of pure hydrogen peroxide is taken as 1.5 (see Abstr., 1895, ii, 346), the application of the mixture rule gives 92.8 as the dielectric constant of pure hydrogen peroxide. The fact that this compound has a considerably greater dielectric constant than water, and that it shows no anomalous electrical absorption, agrees with the views of Brühl, who supposes hydrogen peroxide to contain no hydroxyl groups, and has predicted for it a large dielectric constant on account of free valency (Abstr., 1896, ii, 162; 1897, ii, 198). J. C. P.

Effect of Suspended Particles on Conductivity. By MAX. OKER-BLOM (*Pflüger Arch.*, 1900, 79, 510—533. See this vol., ii, 356).

Electrolytic Conductivity and Internal Friction in Saline Solutions. By P. MASSOULIER (*Compt. rend.*, 1900, 130, 773—775).—Although electrolytic conductivity and internal friction have been found to vary in the same sense, yet no quantitative proportionality has been found, and in almost all the experiments hitherto made the variations of friction have been very slight. The author therefore measured the conductivity and internal frictions of solutions of copper sulphate in water and aqueous glycerol in which great variations of internal friction are obtainable. Determinations were made at 0° and at 15° with the following results for the latter temperature.

Glycerol.	Resistance.	Internal friction.
0	100	100
1/48	104	105
1/24	111	114
1/12	126	132
1/6	161	160
1/3	289	298

The agreement is also stated to be very satisfactory for solutions of the halogen compounds of sodium and potassium. L. M. J.

Conductivity of some Sodium Derivatives of Nitroparaffins. By OTTOKAR ŠULC (*Zeit. physikal. Chem.*, 1900, 32, 625—629).—Nitromethane, nitroethane, nitropropane, and nitroisopropane are found to be compounds of acidic character, for their sodium derivatives in aqueous solution are good conductors. The following results were obtained:

	μ_{1024}	μ_{32}
$\text{CH}_2\text{Na}\cdot\text{NO}_2$	108.6	84.4
$\text{CH}_3\cdot\text{CHNa}\cdot\text{NO}_2$	81.9	69.0
$\text{CH}_3\cdot\text{CH}_2\cdot\text{CHNa}\cdot\text{NO}_2$	80.8	67.8
$\text{C}(\text{CH}_3)_2\text{Na}\cdot\text{NO}_2$	93.1	65.0

The numbers for the last compound are somewhat uncertain.

J. C. P.

Finding the Ionisation of Complex Solutions of given Concentration, and the Converse Problem. By JAMES G. MACGREGOR (*Chem. Centr.*, 1900, i, 390—391; from *Trans. Nova Scot. Inst. Sci.*, 10, 67—78).—Two electrolytes in mixed solution and containing a common ion may be supposed to occupy distinct portions or regions of the solution: on this supposition, the equations are deduced:—(1) $a_1/V_1 = a_2/V_2$; (2) $N_1V_1 + N_2V_2 = 1$; (3) $a_1/V_1 = f_1(V_1)$; (4) $a_2/V_2 = f_2(V_2)$, where a_1 and a_2 are the ionisation coefficients of the two electrolytes, N_1 and N_2 their concentrations, V_1 and V_2 their regional dilutions in litres per gram equivalent. The functions f_1 and f_2 are very complex, and the equations cannot be solved algebraically. The present paper shows how, by a graphic method, the ionisation in a mixed solution may be calculated from the concentrations, and, conversely, how the composition of the solution may be calculated when the degree of dissociation is given. This method of calculation is compared with those of Schrader and Kay.

J. C. P.

Conductivity, Specific Gravity, and Surface Tension of Aqueous Solutions containing Potassium Chloride and Sulphate. By JAMES BARNES (*Chem. Centr.*, 1900, i, 391; from *Trans. Nova Scot. Inst. Sci.*, 10, 49—66).—The methods given by MacGregor for calculating the conductivity (compare previous abstract) and other properties of a mixed solution of two electrolytes have been tested by the author. It is found that the values for the conductivity, sp. gr., and surface tension of mixed solutions of the above-named salts agree within the limits of experimental error with those calculated from the properties of the separate solutions.

J. C. P.

Electrolytic Decomposition Point of Aqueous Solutions. By ALBERT GÖCKEL (*Zeit. physikal. Chem.*, 1900, 32, 607—624).—When a gradually increasing E.M.F. is applied to the electrodes of an electrolytic cell, there is, according to Le Blanc (*Abstr.*, 1891, 1405; 1894, ii, 4), a definite point at which decomposition of the electrolyte begins, as evidenced by a sudden increase of the current passing through the circuit. The author's experiments, made with different

electrolytes and under varying conditions, show that in the curves connecting the applied E.M.F. with the current passing through the cell there is absolutely no distinct break. He regards the so-called E.M.F. of decomposition as in no way characteristic of the particular ion involved, but supposes it to depend on the conditions, and to be the point at which the electrolysis first becomes evident; possibly it is the point at which the products of the electrolysis begin to react with the solvent, the dissolved gases, or the electrode. J. C. P.

Electrolysis of Fused Salts. By RICHARD LORENZ [with A. HELFENSTEIN] (*Zeit. anorg. Chem.*, 1900, 23, 97—110. Compare Abstr., 1900, ii, 61).—An investigation of this subject from the point of view of Faraday's law shows the great importance of keeping the electrodes apart, and indicates the conditions under which trustworthy values of the E.M.F. of polarisation and its temperature coefficient can be obtained (compare Abstr., 1899, ii, 267, 724). The current yield in the electrolysis of fused lead chloride diminishes rapidly as the temperature rises, having the value zero at the boiling point of the salt; this rapid fall is due, not only to the accelerated diffusion of the lead and chlorine vapour in the fused mass, but also to the increasing vapour tension of the lead. At constant temperature, the yield increases with the current density and with the distance between the electrodes; it diminishes as the depth of immersion of the anode increases, whilst it is almost quantitative when the anode is quite separated from the cathode. From the above results, it follows that a tube with the electrodes close together is an unsuitable and uneconomical form of apparatus for the electrolysis of fused salts; in such an arrangement, the longer the experiment lasts the poorer is the percentage yield, owing to the more complete diffusion of the products. J. C. P.

Molecular Susceptibility of the Salts of the Rare Earths. By H. DU BOIS and OTTO LIEBKNECHT (*Ber.*, 1900, 33, 975—977. Compare this vol., ii, 127).—In reply to the criticism of Meyer (this vol., ii, 186), the authors point out that the agreement between the numbers obtained by them and those obtained by Meyer is satisfactory in view of the fact that different methods were employed. It is probable that the observed paramagnetism of the yttrium compounds is in reality due to the presence of erbium compounds. A. H.

Thermal Conductivities of Mixtures and of their Constituents. By CHARLES H. LEES (*Phil. Mag.*, 1900, [v], 49, 286—293).—Three expressions have been used to connect the conductivity of a mixture of two components with the separate conductivities. Of these, one is an expression for the conductivity itself, the second for the inverse, or the resistivity, and the third for the logarithm of the conductivity, each being a simple mixture formula; these formulæ correspond with various modes of disposition of the components in the mixture. In order to test the relative values of the three expressions, the author has compared the calculated values with the found values in the case of the following mixtures, tin-bismuth, water-ethyl alcohol, water-glycerol, water-acetic acid, water-methyl alcohol, glycerol-ethyl

alcohol, vaselin-marble, lard-zinc sulphate; it was found that the conductivity formula is the most, and the logarithmic formula the least, unsatisfactory. The latter gives in general values which are too high, the resistivity formula yields values too low. An empirical formula, $k^n = (p_1 k_1^n + p_2 k_2^n) / (p_1 + p_2)$, gives values in fair accord with the determinations, where n is an arbitrary constant. L. M. J.

Bunsen's Ice Calorimeter. By J. W. MELLOR (*J. Physical Chem.*, 1900, 4, 135—136).—To fill the ice calorimeter with water free from air, the author gives the following method. The calorimeter about one-third full of distilled water is connected with a tube dipping under water contained in a distilling flask with condenser connected to a pump. The calorimeter and flask are heated with the pump in action until the water gives the 'click' of air-free water. The calorimeter is then allowed to cool, and fills with the air-free water.

L. M. J.

Heat of Combustion of very Volatile Liquids. By MARCELLIN P. E. BERTHELOT and MARCEL DELÉPINE (*Compt. rend.*, 1900, 130, 1045—1049).—The following values were obtained by burning the substances in a calorimetric bomb containing oxygen under a pressure of 25 atmospheres:

	Molecular heat of combustion in calories		Heat of
	at constant volume.	at constant pressure.	formation.
Acetaldehyde	278·86	279·16	47·45
Methylal	461·9	462·5	96·4
Methyl formate ...	233·2	233·2	93·4
Ethyl formate ...	391·4	391·7	98·2
Propaldehyde	433·8	434·35	55·55
Acetone	426·3	426·9	63·0

The calculated values for formation from the elements, carbon (diamond), hydrogen (gas), and oxygen (gas) are also given.

H. R. LE S.

Heat of Vaporisation of Nitriles and other Organic Compounds. By WLADIMIR LUGININ (*Chem. Centr.*, 1900, i, 451; from *Arch. sci. phys. nat. Genève*, 9, 5—26).—The constants previously recorded (*Abstr.*, 1899, ii, 354) are supplemented by the following:

Compound.	Specific heat.		Heat of vaporisation.	$\frac{MS}{T}$.
	Limits.	Value.		
Propionitrile ...	19·2—95·1°	0·5378	134·40	19·97
Benzonitrile ...	21 —186	0·4412	87·71	19·47
Acetophenone...	20 —196	0·4744	77·24	19·44
<i>m</i> -Cresol	21 —197	0·5534	100·46	22·86
Acetic acid	22·5—111·4	0·5323	89·79	13·74

In the above table, M is the molecular weight, S the heat of vaporisation, and T the boiling point on the absolute scale. The first three compounds give a value for the expression MS/T approximately = 20, and are therefore not polymerised, although Ramsay and Shields found that propionitrile molecules polymerised. The high value obtained for *m*-cresol points to polymerisation on the part of

this compound. The author finds for the heat of vaporisation of acetic acid a value considerably greater than that (84.9) obtained by Berthelot and Ogier. If 80 be added to the value of S for acetic acid, corresponding with the change from double to single molecules, the expression $MS/T = 26.28$. J. C. P.

Freezing Point of Aqueous Solutions of Non-electrolytes. By ELMER H. LOOMIS (*Zeit. physikal. Chem.*, 1900, 32, 578—606).—The author considers that his earlier method of determining the freezing point of dilute solutions (*Ann. Phys. Chem.*, 1893, [ii], 51, 500) satisfies the condition that the convergence temperature of the apparatus agrees with the true observed freezing point. In the earlier experiments, the thermometer, when not in use, was kept completely surrounded with ice; this procedure is now regarded as an error, as only the lower part of the thermometer should be so preserved.

The author finds the value of van't Hoff's constant in dilute solutions of propyl alcohol, butyl alcohol, amyl alcohol, glycerol, acetone, dextrose, sucrose, mannitol and aniline to be 1.86; abnormal values are found for methyl alcohol (1.82), ethyl alcohol (1.84), and ether (1.50). J. C. P.

Freezing Point Curve for Water containing Hydrogen Chloride and Phenol. By J. A. EMERY and FRANK K. CAMERON (*J. Physical Chem.*, 1900, 4, 130—134).—The freezing point of a saturated aqueous solution of phenol was found to be -1.179° . By the addition of hydrogen chloride, a linear freezing point curve is obtained for dilute solutions, the molecular depression being 3.648, whilst in pure water it was found by Jones to be 3.630. It follows that the effects of the two compounds in producing cryoscopic depression are purely additive. L. M. J.

Minimum Volume of Liquids. By DANIEL BERTHELOT (*Compt. rend.*, 1900, 130, 713—716).—If a curve be drawn with the values of the mean of the densities of liquid and saturated vapour as ordinates, and with temperatures as abscissæ, the result is a straight line, and since at the absolute zero the density of the saturated vapour may be regarded as zero, it follows that by the prolongation of this line the value of the density of the liquid at absolute zero is obtained and hence also the volume which may be regarded as the minimum volume. The minimum volumes so obtained are given for nitrogen, oxygen, chlorine, bromine, carbon dioxide, sulphur dioxide, ethylene, carbon tetrachloride, stannic chloride, ethyl ether, benzene, fluorobenzene, chlorobenzene, bromobenzene, iodobenzene, pentane, isopentane, hexane, and heptane. The examination of these values is deferred, but the author states that the chief point of interest is that if the volumes are measured from these minima and a different zero of temperature be taken for each compound, then the discrepancies from the law of corresponding states disappear (see also Guldberg, this vol., ii, 264; Meyer, this vol., ii, 263). L. M. J.

Dissociation of Dissolved Substances. I. By AD. VANDENBERGHE (*Chem. Centr.*, 1900, i, 391; from *Bull. Acad. med. Belg.*, [iii], 37, 657—679).—Freezing point and boiling point methods give

values for the molecular weight which are often too low on account of dissociation, or too high on account of association. The author, in determining the influence of temperature and concentration on these phenomena, uses chemically similar solvents, namely, methyl, ethyl, and propyl alcohols. The molecular weights of picric acid, naphthalene and carbamide have been determined in these solvents by a boiling point method. The extent of dissociation increases as the boiling point of the solvent rises, and the extent of association increases with the concentration of the dissolved substance.

J. C. P.

Viscosity of Solutions. By R. HOSKING (*Phil. Mag.*, 1900, **49**, 274—286).—The apparatus and method of observation employed were essentially similar to those used by Thorpe and Rodger (*Phil. Trans.*, 1894), and the accuracy of the determinations is seen by the close agreement of the results for water with those of Thorpe and Rodger, Slotte, Sprung, and Poiseuille. Solutions of (1) sodium chloride, and (2) sucrose, were examined, these being selected as typical electrolytic and non-electrolytic solutions; the results are as follows:

(1) Sodium chloride.

Temp.	0 per cent.	5 per cent.	10 per cent.	20 per cent.
0°	0·01794	0·01862	0·02041	0·02666
20	0·01009	0·01083	0·01194	0·01540
50	0·00553	0·00614	0·00680	0·00866
90	0·00320	0·00355	0·00401	0·00507

(2) Sucrose.

	5 per cent.	10 per cent.	20 per cent.	40 per cent.
0°	0·02048	0·02436	0·03720	0·1476
20	0·01139	0·01328	0·01910	0·0607
50	0·00611	0·00699	0·00961	0·02410
90	0·00349	0·00389	0·00511	0·01093

L. M. J.

Drop Methods for the Determination of Molecular Weights. By G. ROSSET (*Bull. Soc. Chim.*, 1900, [iii], **23**, 245—250).—The variation of the surface tension of solutions is proportional to the molecular concentration of the solute, and hence the measurement of the constant is of use for the determination of molecular weights. The author has studied the drop method with the object of finding its availability as a speedy and accurate process. The weights of a hundred drops and also of equal volumes of the solutions were determined, and hence the number of drops in equal volumes can be found. These numbers are inversely proportional to the capillary constants f/d , where f is surface tension and d the density, and vary as a linear function of concentration, so that $1/n_1 = 1/n - kx$ where x is the concentration. In the case of sodium chloride solutions, this expression was verified for concentrations up to 10 per cent. at 23°, and to 30 per cent. at 24°; above 20 per cent., the accord between the determinations and calculated values is not satisfactory, so that the expression does not hold at these high concentrations. It was found that the pressure has a great effect on the number of drops, the weight of 100

drops of water decreasing from 8.192 grams to 7.570 grams when the pressure rose from 29 mm. to 150 mm. of water. The time of dropping was found to be approximately inversely proportional to the pressure. Owing to the great effect of pressure, it is necessary that all experiment for the determination of molecular weights be made at a constant pressure.

L. M. J.

Molecular Association in Liquids. By DANIEL BERTHELOT (*Compt. rend.*, 1900, 130, 565—568).—By the assumption of the law of corresponding states, it is possible from the values of the critical temperature and pressure, and the value of the density at some other temperature and pressure, to calculate the mol. weight of the compound. The ratio of the mol. weight so obtained to the true value is equal to, greater than, or less than unity according as the compound is normal, associated, or dissociated. Thus, for carbon disulphide, values of from 0.96 to 0.97 are obtained, and for ethyl chloride of from 0.98 to 0.99, hence these are normal. For methyl, ethyl, and propyl alcohols, the values are respectively 1.256, 1.115, and 1.116, so that these compounds are associated. It is not found that the values alter with temperature and pressure, so that the factors of association of these compounds are regarded as practically constant through the whole range of the liquid state; water, however, exhibits considerable differences of association.

L. M. J.

Chemical Reactions in Solution: Vapour Tension of the Solvent. By A. PONSOT (*Compt. rend.*, 1900, 130, 782—785).—By the consideration of a cycle of reversible operations in a homogeneous mixture, the author obtains the following deductions. When spontaneous reactions, taking place at constant pressure and temperature amongst dissolved substances or mixtures modify the system, they cause: (1) an increase to a maximum of the vapour pressure of the solvent, if it takes no part in the reaction; (2) an increase of that of a produced compound, and conversely. It also follows that the sense of the chemical change of a system not in equilibrium is independent of the nature of the solvent.

L. M. J.

Equilibrium in the Partition of an Acid between Zinc Hydroxide and Ammonia. By W. HERZ (*Zeit. anorg. Chem.*, 1900, 23, 222—227).—The equilibrium represented by the scheme, $\text{Zn}(\text{OH})_2 + 2\text{NH}_4\text{Cl} \rightleftharpoons \text{ZnCl}_2 + 2\text{NH}_4\text{OH}$, is analogous to that between manganous salts and ammonia (Abstr., 1899, ii, 752; 1900, ii, 68). The law of mass action leads to $K = [\text{Zn} \cdot]^{1/2} / [\text{NH}_4 \cdot]$, but the values of K obtained from this equation are not constant; the relation, $K = [\text{Zn}] / [\text{NH}_4]$, is more nearly satisfied by the results obtained, but the values of the constant diminish slightly with falling concentration. In more dilute solutions, the point of equilibrium was approached from the other side, namely, by adding ammonia to zinc salt solutions; fairly constant values were then obtained for the expression $[\text{Zn} \cdot][\text{NH}_3]^{1/2} / [\text{NH}_4 \cdot]^2$, except when the ammonia was in excess and gave rise to the formation of complex ions. It is immaterial for the equilibrium whether zinc sulphate or zinc nitrate is employed.

From the experiments the solubility of zinc hydroxide is calculated to be 2.6×10^{-5} , agreeing with Bodländer's value 2.5×10^{-5} .

J. C. P.

Decomposition by Sodium of Organic Halogen Compounds dissolved in Amyl Alcohol. By RICHARD LÖWENHERZ (*Zeit. physikal. Chem.*, 1900, 32, 477—493. Compare Abstr., 1899, ii, 639).—Pieces of sodium were added to solutions of iodobenzene, chlorobenzene, benzyl chloride, *isobutyl* iodide, bromobenzene, and *isobutyl* bromide in amyl alcohol; the halogen eliminated and the sodium in solution were subsequently determined by titration. Preliminary experiments showed that the quantity of halogen eliminated was generally proportional (1) to the concentration of the halogen compound, (2) to the quantity of dissolved sodium. This leads to the equation $dx/d(\text{Na}) = k(a - x)$, where (Na) is the dissolved sodium in gram atoms per kilogram of solution, a the initial quantity of halogen compound, x the quantity decomposed; k is a constant. On integration, the equation assumes the form $k = 1/(\text{Na}) \cdot \log_e a(a - x)$. The initial concentration of the halogen compound was in most cases 0.1 gram-mol. per kilogram of solution, and the values of k obtained were satisfactorily constant within the separate series, except in the case of bromobenzene, which, however, gave constant values for k in more dilute solution. For each of the compounds iodobenzene, chlorobenzene, benzyl chloride, and *isobutyl* iodide, k has the same value; for *isobutyl* bromide, it is somewhat smaller. In the case of iodobenzene, k was found to diminish both with rising temperature and with falling concentration of the halogen compound.

J. C. P.

Absorption of Hydrogen Chloride and Potassium Chloride from Aqueous Solution by Colloidal Stannic Oxide. By JACOBUS M. VAN BEMMELN and EDUARD A. KLOBBIE (*Zeit. anorg. Chem.*, 1900, 23, 111—125. Compare Abstr., 1882, 571; 1897, ii, 137; 1899, ii, 12, 84).—Metastannic acid has a very considerable power of absorbing hydrogen chloride from aqueous solution; when equilibrium has been established, the concentration of the hydrogen chloride in the colloid is often greater than that in the aqueous solution. The absorption factor $k = (\text{conc. in colloid})/(\text{conc. in solution})$ is not constant, but is dependent on the concentrations at the point of equilibrium. Metastannic acid has an appreciable power of absorbing potassium sulphate. From solutions of potassium chloride and potassium nitrate, the same colloid absorbs as much salt as makes the concentrations in the colloid and in the solution approximately equal.

J. C. P.

Emission and Absorption of Water Vapour by Colloidal Matter. By PIERRE DUHEM (*J. Physical Chem.*, 1900, 4, 65—122). The author has previously shown that hysteresis plays a very important part in many cases of slow chemical change (Abstr., 1897, ii, 439), and Marchis showed that the variations of the zero in thermometers are due to an expansion hysteresis (Abstr., 1899, ii, 545). The author has investigated theoretically the emission and absorption of aqueous vapour by colloids as an example of hysteresis, and shows that the various phenomena observed by van Bemmelen are in

complete accord with the theoretical deductions (compare Abstr., 1897, ii, 137; 1898, ii, 220; 1899, ii, 12, 84, 487, 599). L. M. J.

Metallic Crystallisation by Electric Currents. By DONATO TOMMASI (*Compt. rend.*, 1900, 130, 565. Compare Tommasina, this vol., ii, 185).—A claim for priority, the author pointing out that, in 1882, he had observed that by the passage of an electric current from silver or copper to platinum through distilled water, a crystalline deposit of the anode metal mixed with oxide was obtained in the tube.

L. M. J.

Formation and Transition of Mixed Crystals of Sodium and Potassium Nitrates, and of Sodium and Silver Nitrates. By D. J. HISSINK (*Zeit. physikal. Chem.*, 1900, 32, 537—563).—From fused mixtures of sodium and potassium nitrates, an interrupted series of mixed crystals is formed, the interval extending from 24—85 mols. per cent. of potassium nitrate at 218°. The existence of mixed crystals is shown by the lowering of the transition temperature of potassium nitrate.

The solidification of fused mixtures of sodium and silver nitrates exemplifies Roozeboom's fourth type (this vol., ii, 132). The freezing point rises gradually from 208·6° for pure silver nitrate to 308° for pure sodium nitrate, with a break at 217·5°, corresponding with 19·5 mols. per cent. of sodium nitrate. To the first part of the freezing point curve there correspond mixed crystals of the AgNO_3 type, containing from 0—26 mols. per cent. of sodium nitrate; to the second part of the curve there correspond mixed crystals of the NaNO_3 type, containing from 38—100 mols. per cent. of sodium nitrate. The interval, 26—38 mols. per cent. of sodium nitrate becomes wider as the temperature falls, and at 138° the limits are 4·5 and ± 50 mols. per cent. of sodium nitrate. The transition temperature of mixed crystals of the AgNO_3 type, as determined by an air dilatometer, falls from 159·8° to 138°, as their molecular composition changes from 0—4 per cent. of sodium nitrate. The gap between mixed crystals of the AgNO_3 type and those of the NaNO_3 type becomes still wider with falling temperature, as shown by solubility experiments in aqueous alcohol; at 15°, the interval extends from 1·6—64·4 mols. per cent. of sodium nitrate.

No transition point could be found for sodium nitrate between +270° and -50°; neither could any sudden transition of the mixed crystals of the NaNO_3 type be detected below 138°. J. C. P.

[**Crystalline Liquids.**] By RUDOLF SCHENCK (*Zeit. physikal. Chem.*, 1900, 32, 564—565).—A reply to Roozeboom's criticisms (*ibid.*, 1899, 30, 428) on the author's work dealing with enantiotropic and monotropic modifications of azoxyanisole (Abstr., 1899, ii, 637).

J. C. P.

Report of the [American] Committee on Atomic Weights. By FRANK W. CLARKE (*J. Amer. Chem. Soc.*, 1900, 22, 70—80).—A résumé of the work published during 1899 on the atomic weights of boron, nitrogen, calcium, nickel, cobalt, molybdenum, tungsten, cerium,

palladium, radium and copper ; a corrected table of the atomic weights of all the elements is appended. E. G.

Lecture Experiment on the Law of Multiple Proportions. By FRIEDRICH EMICH and FRIEDRICH DÖRNER (*Chem. Centr.*, 1900, i, 579—580 ; from *Zeit. phys.-chem. Unterr.*, 12, 281—282).—When lead dioxide is heated, it loses half its oxygen, and by the action of chlorine on the residual monoxide at a red heat, the remainder of the oxygen is liberated. These decompositions are made the basis of a convenient lecture experiment to illustrate the law of multiple proportions. The air is displaced from the tube containing the dioxide by means of carbon dioxide, and the oxygen evolved on heating is measured in a Schiff's nitrometer over potassium hydroxide solution, the last traces of oxygen being finally driven over by means of carbon dioxide. Chlorine is then passed over the residual lead monoxide, which is raised to a red heat, and the oxygen liberated is again measured as before over potassium hydroxide solution. E. W. W.

New Gasometer of Constant Pressure, Adjustable at Will. By JOSEPH RIBAN (*Bull. Soc. Chim.*, 1900, [iii], 23, 222—226).—In its general appearance, this apparatus resembles the ordinary laboratory gasometer, but differs from the latter in having two water reservoirs, an upper exterior one capable of being fixed at any desired height, and a lower interior reservoir in the upper part of the gas container. The gas is delivered at a constant pressure measured by the difference in height between the levels of the water in the two reservoirs. There are also various minor improvements which facilitate the expulsion of air before filling the gasometer with gas and prevent escape of gas or entry of air resulting from alterations in temperature. N. L.

Inorganic Chemistry.

Preparation and Properties of Anhydrous Perchloric Acid.
By DANIEL VORLÄNDER and RUDOLF VON SCHILLING (*Annalen*, 1900, 310, 369—380).—Anhydrous perchloric acid is prepared by distilling potassium perchlorate (50 grams) with 96—97·5 per cent. sulphuric acid (150—175 grams) under 50—70 mm. pressure, and after removing chlorine dioxide by means of a current of air, redistilling the product under the same pressure. The anhydrous acid is colourless, boils at 39° under 56 mm. pressure, and has a sp. gr. 1·764 at 22°/4°; it remains liquid in a mixture of ether and solid carbon dioxide. It does not dissolve in carbon tetrachloride, with which it forms a green emulsion, which soon becomes brown, and evolves hydrogen chloride and phosgene; chloroform, however, dissolves it in every proportion, and on exposing the solution to air, crystals of the monohydrate separate, whilst phosphoric oxide produces a violent explosion. When a few c.c. of benzene are added to a drop or two of perchloric acid, heat is generated, and a brown pre-

precipitate is formed; equal volumes yield a green emulsion, which explodes.

The spontaneous decomposition of anhydrous perchloric acid proceeds when the substance is protected from light and maintained at a low temperature; samples of the purest acid, sealed in glass bulbs, become pale yellow in 2 or 3 days, then gradually brown, and after 3 or 4 weeks the bulbs are shattered by the pressure of the gases evolved in the decomposition.

The authors discuss the action of more concentrated sulphuric acid, and of phosphoric and pyrophosphoric acids on potassium perchlorate.
M. O. F.

Molecular Weight of Sulphur as Determined by the Boiling Point Method. By LOUIS ARONSTEIN and S. H. MEIHZUEN (*Chem. Centr.*, 1900, i, 392—393; from *Arch. néerland. sci. exp. nat.*, [ii], 3, 89—130).—In solutions, sulphur is found to have a molecular weight corresponding with the formula S_8 , whether above or below its transition and melting points. No importance is to be attached to the molecular weight 64 obtained by Orndorff and Terrasse in disulphur dichloride (*Abstr.*, 1896, ii, 358), since this solvent decomposes at its boiling point.
J. C. P.

Sulphur Perfluoride, SF_6 ; a New Gas. By HENRI MOISSAN and PAUL LEBEAU (*Compt. rend.*, 1900, 130, 865—871).—When sulphur is introduced into a vessel containing fluorine, it immediately takes fire, and burns with a livid flame; the product is gaseous, and consists of at least two compounds, for the mixture, although quite insoluble in water, partly dissolves in an aqueous solution of potassium hydroxide. When the fluorine is in excess, the product contains 80—90 per cent. of the insoluble constituent; the inert gas appears, therefore, to be a perfluoride.

The mixture of sulphur fluorides is liquefied by cooling to -80° , freed from foreign gases by fractional distillation, treated with concentrated potassium hydroxide solution, and finally dried over the fused alkali; the perfluoride thus obtained is freed from traces of nitrogen by liquefaction and fractionation, the latter gas passing off in the first portion of the distillate.

Sulphur perfluoride, SF_6 , is a colourless, inodorous, tasteless, combustible gas, which does not support combustion; it is very sparingly soluble in water, dissolving to a slightly greater extent in absolute alcohol; when cooled to -55° , it solidifies to a white, crystalline mass, which melts and boils at slightly higher temperatures. The perfluoride is a very inert gas, resembling nitrogen more than sulphur chloride; potassium hydroxide, whether fused or in alcoholic or aqueous solution, does not act on it, and it is not affected by lead chromate, copper oxide, silver, copper, phosphorus, arsenic, boron, silicon, or carbon, even at a red heat. Fluorine, and the halogens, ammonia, and hydrogen chloride have no action on the gas, even at high temperatures. No change occurs when the gas is heated alone up to the fusing point of hard glass; at the temperature of the induction spark, however, it is partially decomposed, but even after prolonging the action for over 2 hours, 11 per cent. of the perfluoride remains unchanged. When

sparked in the presence of excess of hydrogen, the perfluoride is completely decomposed with the production of hydrogen sulphide and hydrogen fluoride; these compounds, acting on the glass of the containing vessel, form a yellow solid, which consists of sulphur, silica, and hydrofluosilicic acid. A mixture of the perfluoride and oxygen, when strongly sparked, yields a brown, flocculent solid; one part by volume of the latter gas is absorbed, and the total contraction is two volumes; when the current intensity is diminished, the reaction takes a different course, an oxyfluoride of sulphur being produced, which is less rapidly decomposed by water than thionyl fluoride.

When the perfluoride is heated with sulphur vapour in a glass vessel, lower fluorides of sulphur are produced, and these act on the glass, forming silicon fluoride and sulphur dioxide; if the heating is prolonged, the decomposition is complete. Selenium behaves in a similar manner, but the reaction is more complicated, a mixture of silicon fluoride and the dioxides of sulphur and selenium being obtained.

Calcium and magnesium, when heated in the gas, are only superficially attacked; boiling sodium, however, rapidly absorbs the perfluoride. When the gas is heated with hydrogen sulphide, the following reaction takes place: $\text{SF}_6 + 3\text{H}_2\text{S} = 6\text{HF} + 4\text{S}$; the hydrogen fluoride immediately attacks the glass of the vessel, so that hydrofluosilicic and silicic acids are the ultimate products.

The paper contains a description of the apparatus employed in preparing the mixed fluorides.
G. T. M.

Density and Analysis of Sulphur Perfluoride. By HENRI MOISSAN and PAUL LEBEAU (*Compt. rend.*, 1900, 130, 984—988).—The gaseous sulphur perfluoride (preceding abstract) has a sp. gr. 5.03 (air=1); its analysis was effected by heating it with sodium vapour, a mixture of sodium sulphide and fluoride being thus obtained, and also by heating with sulphur in glass vessels, and measuring the volume of the silicon fluoride and sulphur dioxide produced. The perfluoride was also decomposed by heating with selenium. The results thus obtained are in close agreement with the formula SF_6 .
N. L.

Sulphuric Acid containing Selenium. By CHARLES F. SCHLAGDENHAUFFEN and C. PAGEL (*J. Pharm.*, 1900, [vi], 11, 261—262).—A large number of samples of so-called "pure" sulphuric acid were found to contain selenium; a very delicate test for the latter consists in adding a fragment of codeine to 4 or 5 drops of the concentrated acid, when a green coloration is produced in the cold, which changes to bluish-green at 100°.
W. A. D.

Passage of Argon through Thin Films of Indiarubber. By LORD RAYLEIGH (*Phil. Mag.*, 1900, [v], 49, 220—221).—Air was allowed to diffuse into an indiarubber balloon, and the composition of the contents then determined; it was found that the argon now formed 1.93 per cent. of the argon and nitrogen, whilst corresponding percentage for air itself was 1.19. Argon, therefore, passes through indiarubber more readily than nitrogen, but not in such a degree as to render the process suitable for the concentration of argon from the atmosphere.
L. M. J.

Electrolysis of Alkali Chloride Solutions with a Diaphragm. By FRITZ FOERSTER and F. JORRE (*Zeit. anorg. Chem.*, 1900, 23, 158—219).—Theoretical considerations show that the yield of chlorine obtained in the electrolysis of neutral alkali chloride solutions will in general be less than the yield of alkali, so long as the existence of hypochlorite in the anode solution is possible (compare this vol., ii, 72). When a diaphragm is used, the nature of the process depends on three factors—the ordinary electrical conduction in the diaphragm, the diffusion, and the electrical endosmose.

Experiments with a platino-iridium anode, in which the anode and cathode solutions were analysed after the electrolysis, showed that the total yield of alkali diminishes with increasing concentration of the alkali hydroxide. The yield of chlorine was found to be less than the yield of alkali, especially in the first stages of the electrolysis; the difference vanished later on when the chlorate and hydrogen chloride concentrations became appreciable. The chloride concentration, owing to the electrical endosmose, falls much more slowly in the cathode solution than in the anode solution. Analysis of the anode solution after electrolysis indicated the presence of free hypochlorous acid and alkali chlorate, but not of alkali hypochlorite. The proportion of oxygen liberated at the anode increases regularly with the progress of the electrolysis.

When carbon anodes are used, the process of electrolysis is essentially the same; the gas liberated at the anode contains carbon dioxide, and hydrogen chloride is found in the anode solution at a higher alkali chloride concentration than when platino-iridium anodes are used.

Solutions of potassium chloride give a better current yield than those of sodium chloride; this is connected partly with the greater dissociation of the former salt, and the greater velocity of migration of the potassium ion.

J. C. P.

Production of Iodated Potassium and Ammonium Carnallites. By AUGUST DE SCHULTEN (*Bull. Soc. Chim.*, 1900, [iii], 23, 158—159. Compare Abstr., 1898, ii, 512).—Substituted carnallites of the formulæ $\text{KI}, \text{MgI}_2 + 6\text{H}_2\text{O}$ and $\text{NH}_4\text{I}, \text{MgI}_2 + 6\text{H}_2\text{O}$ are obtained when solutions of the mixed salts are left to evaporate over sulphuric acid in a vacuum. The crystals form flattened prisms, are very hygroscopic, and have respectively the sp. grs. 2.547 and 2.346 at 15°

N. L.

Action of Chlorine on Metallic Silver in the Light and in the Dark. By V. VON CORDIER (*Monatsh.*, 1900, 21, 184—199).—The action of chlorine on pure silver has been tried under varying degrees of illumination, and it is found that (i) dry chlorine has no action, either in the light or in the dark; (ii) moist chlorine has a weak action, which, within certain limits, varies with the intensity of the light; (iii) illumination of the chlorinated silver in a stream of an indifferent gas causes a decrease in weight of the silver, probably due to a decomposition of the silver chloride; (iv) an intense illumination of the chlorine before contact with the silver causes an increased absorption; (v) electric sparking of the chlorine has the same effect.

Copper, treated under similar conditions to silver, gives different results. R. H. P.

Reducing Action of Calcium Carbide. By H. CHR. GEELMUYDEN (*Compt. rend.*, 1900, 130, 1026—1029).—Boric oxide reacts with calcium carbide, at the temperature of the electric furnace, to form calcium boride, CaB_6 . Under the same conditions, the sulphides of iron, lead, antimony, and magnesium are also reduced, the metals being completely volatilised, except in the case of iron. Aluminium sulphide is not reduced by calcium carbide. N. L.

Hydrated Barium Peroxides. By ROBERT DE FORCRAND (*Compt. rend.*, 1900, 130, 778—780; 834—837).—The results given in the first of these papers are incorrect, the heat of dissolution of hydrated barium hydroxide having been taken as +14.1 Cal. instead of -14.1 Cal.; the correct figures are given in the second paper. Experiments with various proportions of hydrogen peroxide and barium oxide lead to the conclusion that $\text{BaO diss.} + \text{H}_2\text{O}_2 \text{ diss.} = \text{BaO}_2 \text{ ppt.} + \text{H}_2\text{O}$ develops +25.497 Cal., whilst the dissolution of the peroxide in dilute hydrochloric acid develops +2.723 Cal. These results differ somewhat from the earlier results of Berthelot.

The barium peroxide obtained in this manner is never quite free from monoxide, but, contrary to the general belief, the proportion of peroxide is highest when the barium monoxide, and not the hydrogen peroxide, is in excess.

The conversion of the peroxide into the trioxide, and of the latter into the tetroxide, by the action of a large excess of hydrogen peroxide, seems to be accompanied by no appreciable thermal disturbance. The conversion is, as a rule, incomplete, and the composition of the product varies with the conditions. C. H. B.

Heat of Formation of Hydrated and Anhydrous Strontium Dioxide. By ROBERT DE FORCRAND (*Compt. rend.*, 1900, 130, 1017—1019).—The heat of formation of the precipitated, hydrated dioxide, $\text{SrO}_2 + 9\text{H}_2\text{O}$, obtained by mixing solutions of the monoxide and hydrogen peroxide, is 26.576 Cal., which is about 1 Cal. higher than the corresponding figure for barium dioxide (preceding abstract); its heat of dissolution in hydrochloric acid is 1.744 Cal. The heat of dissolution of the anhydrous dioxide in hydrochloric acid is 22.225 Cal., whence it is calculated that the heat of formation of the dioxide from the solid monoxide and gaseous oxygen is 10.875 Cal., whilst its heat of hydration is 20.481 Cal. (liquid water) and 7.611 Cal. (solid water). Comparison of these figures with the heat of formation (12.10 Cal.) and hydration (18.20 Cal.) of barium dioxide explains why anhydrous strontium dioxide is less stable and less easy to obtain free from monoxide than the barium compound, whereas, with the hydrated dioxides, the relative stability is reversed. N. L.

Reactions of Magnesium, Zinc, and Iron with Solution of Cupric Sulphate. By ROBERT M. CAVEN (*J. Soc. Chem. Ind.*, 1900, 19, 18—22. Compare *Proc.*, 1897, 13, 221; 1898, 14, 57).—The action of magnesium, zinc, and iron on solutions of copper sulphate is not one of simple displacement of copper by the other metal only, but

is attended with several complicated reactions, such as evolution of hydrogen, formation of cuprous oxide, basic cupric sulphate, cuprous sulphate, and even free sulphuric acid ; also of oxides, or basic sulphates of magnesium, zinc, or iron.

The experiments have been conducted with solutions of copper sulphate of varying strength and at different temperatures, and the results are tabulated.

L. DE K.

Influence of Ammonia on Magnesium Salts. By W. SCHIEBER (*Chem. Centr.*, 1900, i, 652 ; from *Oesterr. Chem. Zeit.*, 3, 83—84).—The addition of ammonia to a solution of a magnesium salt containing as much as 4 mols. of ammonium salt to 1 mol. of magnesium salt will often cause the solution to become turbid, and on boiling a precipitate is always formed. The prevention of the precipitation of magnesium hydroxide by means of ammonium salts is not only dependent on the relative quantities of the ammonium and magnesium salts present, but also on the amount of free ammonia added, and possibly also on the concentration, hence, in separating alumina from magnesia, a considerable quantity of ammonium chloride is required, but the ammonia added should be reduced to a minimum.

E. W. W.

Electrolytic Deposition of Brass. By J. LIVINGSTON R. MORGAN (*J. Amer. Chem. Soc.*, 1900, 22, 93—99).—The theory of this operation is discussed. For the deposition of brass, it is necessary (1) that the solution contain zinc and copper ions in such a proportion that $P/p : P_1/p_1 :: 30 : 70$, where P and P_1 are the electrolytic solution pressures of zinc and copper, p and p_1 the osmotic pressures of their ions in the solution ; (2) that the solution contain complex ions of zinc and copper. From solutions of their simple salts, the metals would not be deposited in the requisite proportion ; this would change the composition of the liquid, and the zinc and copper of the anode would no longer dissolve in the required ratio. Further, (3) the maximum concentration of copper ions should be as small as possible, in order that copper may be easily dissolved from the anode.

The above conditions are fulfilled by a solution of the mixed zinc and copper salts in potassium cyanide. From such a solution, containing as it does the complex ions $\text{Zn}(\text{CN})_4^-$ and $\text{Cu}(\text{CN})_4^-$, zinc and copper may be deposited in varying proportions according to the current density.

J. C. P.

Zinc Selenide and its Dimorphism. By HENRI FONZES-DIAON (*Compt. rend.*, 1900, 130, 832—834).—Zinc selenide obtained by the action of zinc chloride vapour on a mixture of nitrogen and hydrogen selenide crystallises in long, rhombohedral needles carrying, laterally, hemimorphic hexagonal prisms, or in rhombohedra with striated faces, which act strongly on polarised light. The selenide obtained by the action of hydrogen on the selenate also crystallises in long needles belonging to the hexagonal system, whereas, when prepared in the electric furnace, the crystals are optically inactive, and seem to belong to the cubic system, like the crystals obtained by Margottet by heating the amorphous selenide

in hydrogen. The dimorphism of zinc selenide is therefore established, and is analogous to that of the sulphide.

Hexagonal cadmium selenide has been prepared in a similar way.
C. H. B.

Production of Cadmium Vanadinites. By AUGUST DE SCHULTEN (*Bull. Soc. Chim.*, 1900, [iii], 23, 159—160).—*Cadmium chlorovanadinite*, $3\text{Cd}_3(\text{VO}_4)_2\cdot\text{CdCl}_2$, is obtained by heating to fusion a mixture of cadmium chloride, cadmium carbonate, and vanadium pentoxide, in the form of long, hexagonal prisms having a sp. gr. 5.264 at 15°. The crystals are readily soluble in dilute acids, and melt and decompose when heated to redness. *Cadmium bromovanadinite*, $3\text{Cd}_3(\text{VO}_4)_2\cdot\text{CdBr}_2$, obtained in a similar manner from cadmium bromide, closely resembles the chlorovanadinite; it has a sp. gr. 5.456 at 15°. The corresponding iodine compound could not be obtained in a pure state.
N. L.

Action of Hydrogen on Mercury Selenide and the Inverse Action. By H. PÉLABON (*Bull. Soc. Chim.*, 1900, [iii], 23, 211—216).—Mercury selenide is attacked by hydrogen at temperatures above 400° with the production of hydrogen selenide and mercury, the reaction being limited by the inverse action of hydrogen selenide on mercury. The proportion of hydrogen selenide found in the gaseous products of the reaction increases with the temperature and with a diminution of the initial pressure. Thus, at 540° with an initial pressure of 760 mm. equilibrium is attained when 15 per cent. of hydrogen selenide is present, whilst at 440° only 0.52 per cent. is formed. On the other hand, with initial pressures of about 380 mm. and 190 mm. at 540°, the percentages of hydrogen selenide formed become 19 and 27 respectively. These results are shown to be in accordance with thermodynamical reasoning.
N. L.

Formation of Mercuriammonium Iodide by the Regulated Action of Concentrated Ammonia on Mercuridiammonium Iodide. By MAURICE FRANCOIS (*Compt. rend.*, 1900, 130, 1022—1024). When a solution of ammonia of sp. gr. 0.923 is added in large quantity to mercuridiammonium iodide, dimercuriammonium iodide is formed (this vol., ii, 208, 280), but if the ammonia is added slowly and in small portions at a time, mercuriammonium iodide, NH_2HgI , is obtained. The reaction is limited and reversible, since the new compound is reconverted into mercuridiammonium iodide by the action of ammonia and ammonium iodide. Mercuriammonium iodide is a white, crystalline substance, which does not redden on exposure to air and is insoluble in ether.
N. L.

Separation of Rare Earths. By G. URBAIN (*Ann. Chim. Phys.*, 1900, [vii], 19, 184—274).—A detailed account of the fractionation of the rare earths from *æschynite* and *monazite* by methods which have been previously indicated (compare *Abstr.*, 1897, ii, 318; 1898, ii, 518; 1899, ii, 28, 424, 789).
G. T. M.

Separation of the Rare Earths. By R. CHAVASTELON (*Compt. rend.*, 1900, 130, 781—782).—On adding a neutral solution of the salts of cerium, lanthanum, didymium, and thorium to a saturated

solution of sodium sulphite, the last named element remains in solution whilst the others are precipitated as sulphites; the separation is practically complete, the thorium solution containing only traces of the other elements. The mixed sulphites are dissolved in hydrochloric acid and the trace of thorium carried down with these salts is precipitated by treating the solution of the chlorides with hydrogen peroxide; the oxides of the other metals, precipitated from the filtrate by ammonia, are suspended in a solution of an alkali hydrogen carbonate saturated with carbon dioxide, when the cerium oxide dissolves forming a brown solution, the operation being repeated with fresh quantities of the hydrogen carbonate until the residue no longer develops a brown coloration with hydrogen peroxide. The residue now consists of the double sodium carbonates of lanthanum and didymium; the cerium separates in the form of a light yellow precipitate on adding an alkali hydroxide to the brown solution or as an orange-brown precipitate on adding hydrogen peroxide. The latter precipitate dissolves in acids with evolution of carbon dioxide and when hydrochloric acid is employed chlorine is also evolved; the solutions obtained in the cold are yellow and are rendered colourless on warming; these reactions indicate that the compound is a ceric carbonate.

As an alternative method of separation, the oxides of the four elements, obtained by adding ammonia and hydrogen peroxide to solutions of their chlorides, are treated with a solution of an alkali hydrogen carbonate, the peroxides of cerium and thorium dissolve forming a brown solution and the separation of these metals may be effected by either of the following processes: (1) reduction of the peroxides and formation of the sulphites by the action of sulphurous acid and the precipitation of thorium by hydrogen peroxide from a hydrochloric acid solution of these salts; (2) reduction of the brown solution of ceric and thoracic carbonates with sulphurous acid in the presence of sufficient sodium carbonate to keep the whole of the thorium dissolved as the double sodium sulphite. In the latter process, the solution must be constantly agitated during the addition of the sulphurous acid in order to prevent the formation of acid sulphite, otherwise some of the cerium will be dissolved whilst traces of thorium will be precipitated.

G. T. M.

New Method of Fractionating some Rare Earths. By EUGÈNE DEMARCAZ (*Compt. rend.*, 1900, 130, 1019—1022).—The method consists in the fractional crystallisation of the double nitrates of magnesium and the rare earths from nitric acid of sp. gr. 1.3. These salts have the general formula $M_2(NO_3)_6 \cdot 3Mg(NO_3)_2 \cdot 24H_2O$, and are formed by lanthanum, cerium, and the other earths up to holmium, but not by yttrium; their solubility increases with the molecular weight.

N. L.

Austrium. By RICHARD PRIBRAM (*Monatsh.*, 1900, 21, 148—155. Compare Abstr., 1886, 773).—The orthite investigated by Linnemann (*loc. cit.*) has been re-examined by the author, who agrees with Lecoq de Boisbaudran (*Compt. rend.*, 1886, 102, 1436) that Linnemann's "austrium" is identical with gallium. However, from a minute

spectroscopic examination of the mineral, he comes to the conclusion that it contains a new element yet to be isolated. This is provisionally named *austrium*, although it is quite distinct from the element described originally by Linnemann. R. H. P.

New Hydrate of Alumina. By V. ZUNINO (*Gazzetta*, 1900, 30, i, 194—199).—When aluminium is immersed in mercury and afterwards exposed to moist air, a voluminous, greyish, spongy mass is formed on the surface of the metal; the author shows that this substance consists essentially of a *hydrated alumina*, of the composition $\text{Al}_2\text{O}_3 + 5\text{H}_2\text{O}$, small quantities of aluminium, iron, and carbon being also present. This compound is also formed by the action of amalgamated aluminium on water, large quantities of hydrogen being evolved at the same time. T. H. P.

Natural and Artificial Pozzuolana. By GIOVANNI GIORGIS and UGO ALVISI (*Gazzetta*, 1899, 29, i, 185—263, and 1900, 30, i, 96—125).—A bibliographical and historical paper, treating of the subject under the four heads: 1. Natural volcanic and non-volcanic pozzuolana. 2. Artificial pozzuolana. 3. Technical notes on pozzuolana. 4. The principal theories concerning the setting of hydraulic cements. The first three of these divisions are here considered. T. H. P.

A Crystallised Selenide and an Oxselenide of Manganese. By HENRI FONZES-DIACON (*Compt. rend.*, 1900, 130, 1025—1026).—Cubical crystals of manganese selenide, MnSe , are obtained by the action of hydrogen selenide on a solution of manganese acetate containing a small quantity of hydrochloric acid, by reducing manganese selenate with carbon in the electric furnace, or by fusing the precipitated selenide at a high temperature. Prismatic crystals of the same composition are produced by the action of hydrogen selenide on manganese chloride at a red heat. Crystallised manganese selenide has a sp. gr. 5.59 at 15° , is slightly acted on by water at 100° , and is readily attacked by dilute acids; treatment with hydrogen peroxide converts it into manganese selenate.

Manganese selenate is reduced by hydrogen at a bright red heat with the formation of a green oxselenide, analogous to the oxysulphide which is formed by a similar reaction. N. L.

Iron Carbonyls and their Importance in the Industrial Application of Water-Gas. By M. VAN BREUKELEVEEN and A. TER HORST (*Rec. Trav. Chim.*, 1900, 19, 27—32).—Gaseous mixtures containing carbon monoxide have a marked action on iron even under the ordinary pressure. A sample of producer gas containing 37 per cent. of the monoxide, after remaining for 1 week in contact with a polished iron surface, yields a large amount of a volatile iron compound. When the percentage of carbon monoxide is low, the action is inappreciable; a sample of coal gas containing only a small amount of this oxide remained quite free from iron carbonyl after a week's exposure to iron surfaces. The producer gas may be freed from iron carbonyl by passing it over copper heated to 300° , or over moistened potassium permanganate. G. T. M.

Constitution and Genesis of Iron Sulphates. By RUDOLF SCHARIZER (*Zeit. Kryst. Min.*, 1900, 32, 338—354).—Compare Abstr., 1899, ii, 30).—The second paper of this series deals with the action of solutions of various strengths of normal ferric sulphate on ferric hydroxide and on precipitated basic ferric sulphate. In both cases, there are obtained solutions of basic ferric sulphate, $\text{Fe}_2\text{S}_2\text{O}_9$, which is decomposed when the solution is diluted or warmed. L. J. S.

Nickelous Arsenide. By ALBERT GRANGER and GASTON DIDIER (*Compt. rend.*, 1900, 130, 914—915. Compare Abstr., 1894, ii, 392; 1896, ii, 602).—A *nickelous arsenide* having the formula Ni_3As_2 is produced by heating the finely divided metal at 600° in the vapour of arsenious chloride; the compound thus obtained forms reddish, crystalline granules having a metallic lustre and resembling the impure arsenide isolated by Wöhler from smalt residues. Although the arsenide differs in composition from the phosphide, Ni_2P , obtained under similar conditions, it resembles this compound in its chemical properties, being decomposed by heat, soluble in nitric acid and aqua regia, and readily attacked by chlorine and fused alkalis. G. T. M.

Decomposition of Nickel Carbonyl in Solution. By VICTOR LENHER and HERMANN A. LOOS (*J. Amer. Chem. Soc.*, 1900, 22, 114—116).—By the action of moisture on solutions of nickel carbonyl in organic solvents, a green precipitate is produced similar to that furnished by the pure substance in contact with water or moist air. Berthelot (Abstr., 1892, 279) considered this product to be nickelous hydroxide free from carbon, whereas, according to Mond (*J. Soc. Chem. Ind.*, 1892, 11, 750), it is a nickel carbonate of varying composition. The present authors show that it is a decomposition product containing nickel carbonyl and nickelous hydroxide; analysis of a specimen from a toluene solution gave results which point to the composition $\text{Ni}(\text{CO})_4 \cdot 2\text{Ni}(\text{OH})_2 \cdot 4\text{H}_2\text{O}$. E. G.

Nature of the Change from Violet to Green in Solutions of Chromium Salts. By FRANCIS P. VENABLE (*J. Amer. Chem. Soc.*, 1900, 22, 111—114).—A reply to Whitney (this vol., ii, 211), in which the author accepts his results as conclusive. E. G.

Double Carbonates of Chromous Oxide; Saline Oxide of Chromium. By GEORGES BAUGÉ (*Ann. Chim. Phys.*, 1900, [vii], 19, 158—184).—A *résumé* of work already published. Compare Abstr., 1896, ii, 426; 1898, ii, 294, 592; 1899, ii, 157). G. T. M.

New Method for the Preparation of Double Sulphates of Chromium. By C. PAGEL (*Compt. rend.*, 1900, 130, 1030—1032).—When, as in toxicological investigations, the destruction of organic matter is effected by heating with sulphuric acid and potassium dichromate, the double sulphate, $\text{Cr}_2(\text{SO}_4)_3 \cdot 3\text{K}_2\text{SO}_4$, is produced, whilst if sodium dichromate is employed the analogous sodium salt is obtained. Both compounds crystallise in the hexagonal system, the potassium salt in green plates, and the sodium salt in green prisms. A sodium salt of the same composition, but crystallising in pale green,

slender needles is obtained by heating together sodium hydrogen sulphate, ammonium sulphate, and chromium sulphate. N. L.

Tungsten Diphosphide. By ED. DEFACQZ (*Compt. rend.*, 1900, 130, 915—917).—*Tungsten diphosphide*, WP_2 , produced by heating tungsten hexachloride at 450° in a current of hydrogen phosphide, forms a black, crystalline mass insoluble in water and the ordinary organic solvents, and having a sp. gr. 5.8. Fluorine attacks the diphosphide at temperatures above 100° , forming phosphorous and tungsten fluorides; chlorine and bromine react similarly at a red heat; when liquid chlorine is employed at 60° , a chlorophosphide is produced. Sulphur and nitrogen both displace the phosphorus from this compound at high temperatures, forming the disulphide and nitride respectively; the disulphide is also produced by the action of hydrogen sulphide on the phosphide at 500° . The diphosphide readily burns in air or oxygen, forming tungstic and phosphoric oxides, its combustion in the latter gas being attended by a very dazzling flame. A complete reduction of the phosphide is effected by heating it with copper or zinc, tungsten being liberated, and the corresponding metallic phosphide produced; the reduction by hydrogen commences at 525° , but is incomplete even at 900° .

Lead at 900° only partially reduces the diphosphide, and copper phosphide at 1400° produces another tungsten phosphide; when heated with iron, the diphosphide is converted into a double *iron tungsten phosphide*; with aluminium, the reaction is even more complicated, and the product contains a large amount of silicon derived from the crucible. Hydrofluoric and hydrochloric acids do not act on the diphosphide, but a mixture of the former with nitric acid dissolves this compound even in the cold, whilst aqua regia decomposes it on warming; sulphuric and nitric acids, when heated, are reduced by the phosphide, sulphurous acid and blue tungsten oxide being formed in the first case, and nitrous and tungstic acids in the second. The diphosphide is dissolved by fused caustic alkalis and potassium hydrogen sulphate, and is even more readily attacked by heated mixtures of alkali nitrates and carbonates. G. T. M.

Paratungstates. By L. A. HALLOPEAU (*Ann. Chim. Phys.*, 1900, [vii], 19, 92—144).—A *résumé* of work already published (compare Abstr., 1895, ii, 503; 1896, ii, 607; 1897, ii, 178, 498; 1898, ii, 540; 1899, ii, 32, 158, 159, 555). G. T. M.

Actinium: A New Radio-active Element. By A. DEBIERNE (*Compt. rend.*, 1900, 130, 906—908).—The new radio-active element, *actinium*, belonging to the iron group (compare this vol., ii, 20), may be obtained in a more concentrated form by submitting the substances containing it to the following operations: (1) Addition of excess of sodium thiosulphate to solutions slightly acidified with hydrochloric acid; (2) action of hydrofluoric acid and potassium fluoride on the freshly precipitated hydroxides suspended in water; (3) oxidation of neutral solutions of the nitrates by hydrogen peroxide; (4) precipitation of insoluble sulphates. In every case, the precipitate or residue is strongly radio-active, and contains nearly the whole of the actinium;

the second process serves to separate this substance from titanium. The element itself has not been isolated from these mixtures, and in all probability the above reactions are not peculiar to actinium, the radio-active substance being precipitated along with other insoluble compounds, just as ferric oxide is carried down by barium sulphate. By a methodical application of these processes, however, the greater portion of the new element may be extracted from pitchblende.

Chemical and spectroscopic examination of the most active fractions indicates that the predominant element is thorium. Unlike radium or polonium, the new element is not affected by the precipitants for barium or bismuth.

The rays emitted by actinium produce the same effects as those from radium and polonium; a portion of the rays is deflected in a strong magnetic field, the deviation being in the same sense as that of the radium and cathode rays; actinium induces permanent radio-activity on substances placed in its vicinity; its inductive action is, however, very feeble.

Actinium seems to resemble thorium in its chemical properties, and the slight radio-activity exhibited by compounds of the latter may possibly be due to the presence of the former substance. G. T. M.

Thorium Salts. By ARTHUR ROSENHEIM and JOHANNES SCHILLING (*Ber.*, 1900, 33, 977—980).—When thorium hydroxide is washed with alcohol, dissolved in alcoholic hydrogen chloride, and evaporated under diminished pressure, the *hydroxychloride*, $\text{ThCl}_2(\text{OH})_2 + 8\text{H}_2\text{O}$, crystallises in slender, white, hygroscopic needles. The mother liquor from these yields the normal *chloride*, $\text{ThCl}_4 + 9\text{H}_2\text{O}$, which forms well developed crystals and slowly deliquesces. A *hydroxychloride* of the formula $\text{OH} \cdot \text{ThCl}_3 + 11\text{H}_2\text{O}$ is obtained when the solution of the hydroxide in alcoholic hydrogen chloride is evaporated almost to dryness, and the residue treated with aqueous hydrochloric acid. It has been found impossible to obtain the compound of thorium chloride with hydrogen chloride, H_2ThCl_6 , in the free state, but a stable pyridine salt of this acid has been prepared, $(\text{C}_5\text{H}_5\text{N})_2\text{H}_2\text{ThCl}_6$, which forms a compact, crystalline crust.

Thorium hydroxybromide, $\text{ThBr}_2(\text{OH})_2 + 11\text{H}_2\text{O}$, forms small, quadratic crystals, whilst the *bromide*, $\text{ThBr}_4 + 7\text{H}_2\text{O}$, crystallises in well-developed needles. *Pyridine thoribromide*, $(\text{C}_5\text{H}_5\text{N})_2\text{H}_2\text{ThBr}_6$, closely resembles the corresponding chloride, but soon decomposes with evolution of hydrogen bromide.

Chlorides of thorium containing $8\text{H}_2\text{O}$ and $7\text{H}_2\text{O}$, and bromides containing $8\text{H}_2\text{O}$ and $10\text{H}_2\text{O}$ have been described previously. A. H.

A Radio-active Substance Emitted from Thorium Compounds. By E. RUTHERFORD (*Phil. Mag.*, 1900, [v], 49, 1—14).—Schmidt has shown that thorium emits radiations analogous to those emitted by uranium (*Abstr.*, 1898, ii, 550). The author finds that when the radiations proceed from thin layers of thorium oxide, they may be almost completely cut off by a few sheets of paper; but if thick layers of thorium oxide are employed, the radiations are but slightly affected, even by many layers of paper, and further, that the inconstancy of the intensity of the radiations is due to air currents.

The author considers that the radio-activity is due to two causes, (1) radiations, and (2) an emanation which passes away from the oxide, and is capable of passing through paper or metals in thin sheets, but is stopped by mica. This emanation may be carried away by air currents, and the intensity of the radio-activity *slowly* falls, being reduced to about one-half its value in one minute; it passes through cotton-wool without loss of its activity, and may be bubbled through hot or cold water or sulphuric acid; in this respect, it differs from ions. It can affect photographic plates, causes ionisation of gases, and does not appear to be affected by the nature of the surrounding gas. The nature of the emanation is doubtful, as it does not appear to consist of fine dust particles, whilst if a vapour it is insufficient to cause any change in the spectrum of a Plücker vacuum tube. L. M. J.

Radio-activity produced in Substances by the Action of Thorium Compounds. By E. RUTHERFORD (*Phil. Mag.*, 1900, [v], 49, 161—192).—Thorium compounds, especially the oxide, not only possess the property of emitting radiations, but also produce radio-activity in substances placed near them, and in an electric field the radio-activity is chiefly produced, and may be concentrated, upon negatively electrified bodies. This radio-activity is most probably due, not to the radiations from thorium, but to the 'emanation' (preceding abstract), as both emanation and the power of producing radio-activity are removed by air currents and destroyed by high temperatures, whilst further, the intensity of the excited radio-activity is found to be proportional to the current due to the emanation. The radio-activity is independent of the nature of the substance upon which it is produced, metals, wood, and paper being equally affected, and appears to be a surface effect; its intensity falls very slowly, being reduced to about one-half in 11 hours after removal from the influence of the thorium. It decreases with the pressure at low pressures, but is practically constant above about 16 mm., and varies little with the nature of the gas. No dust could be observed to be deposited on excited wires when microscopically examined, neither was any increase of weight found; the activity is not destroyed by heating, but may be removed by long scouring with emery cloth. It is rapidly destroyed by hydrochloric or sulphuric acid, but is only slowly removed by hot or cold nitric acid or sodium hydroxide, and still remained after the electric deposition of a film of copper on the wire. Further, when destroyed by hydrochloric or sulphuric acid, the residue from the acid after evaporation is strongly radio-active. The question as to whether this activity is due to the deposition of positive ions or to that of radio-active particles of the emanation is shortly discussed, although neither view is completely satisfactory (see also Curie, this vol., ii, 126).

L. M. J.

Action of Hydrogen on Antimony Sulphide. By H. PÉLABON (*Compt. rend.*, 1900, 130, 911—914).—The paper deals with the study of the balanced reaction $\text{Sb}_2\text{S}_3 + 3\text{H}_2 = 3\text{H}_2\text{S} + 2\text{Sb}$ at temperatures above 360° , the reagents being contained in sealed tubes. When the temperature is below the melting point of the sulphide, the product consists of a mixture of two solids in contact with a gaseous mixture,

and from the laws of chemical statics the final composition of the gas should be independent of the pressure and of the mass of the solids, and should depend only on the temperature. In order to verify this conclusion, varying quantities of stibnite were heated with hydrogen for 30 hours at constant temperatures; the tubes were then rapidly cooled, the gas analysed, and the results expressed in terms of the partial pressure of hydrogen sulphide in the gaseous mixture. The weight of stibnite and the initial pressure of the hydrogen were varied considerably, but at 440° the partial pressure was practically the same in every case, the extreme values being 42.98 and 43.6; this result was not affected by the preliminary addition of varying amounts of antimony, the mean of four experiments being 43.29. When the temperature is above the melting point of antimony sulphide, this compound dissolves the liberated antimony, so that in this case the equilibrium is established between two homogeneous systems. The final composition of the gas should now depend on the concentration of the solution of antimony in antimony sulphide, and therefore on the amount of stibnite originally present. The experimental results entirely justify this conclusion; at 610° , the amount of hydrogen sulphide increases as the weight of stibnite employed diminishes.

If an excess of antimony is present, the solution of the metal in its sulphide is always saturated, and in this particular case, providing that all the sulphide is not decomposed, the amount of hydrogen sulphide produced should depend solely on the temperature; in accordance with this generalisation, it is found that the factor determined increases with the temperature, being 48.6 at 510° and 56.92 at 625° . When hydrogen sulphide is left in contact with antimony in sealed tubes at constant temperatures, a certain amount of the gas is decomposed, and if the temperature is below the melting point of the metal, the limiting value of the partial pressure is identical with the factor obtained by treating stibnite with hydrogen at the same temperature. If, however, the antimony has melted, the value obtained for the partial pressure is lower than that observed in the inverse reaction; the discrepancy is probably due to the solution of the sulphide in the fused metal.

When the four substances are all present in the system studied, the value of the factor increases with the temperature, and supposing that, as at 15° , the direct reaction is accompanied by an absorption of heat, the experimental results are in complete agreement with the law relating to the variations of chemical equilibrium produced by changes of temperature.

G. T. M.

Crystallised Bismuth Salts. By AUGUST DE SCHULTEN (*Bull. Soc. Chim.*, 1900, [iii], 23, 156—158).—Three grams of bismuth oxide are dissolved in 300 c.c. of hydrochloric acid of sp. gr. 1.05, and the solution mixed with 2.5 litres of boiling water, filtered, and left to cool, when bismuth oxychloride, BiOCl , separates in colourless, quadratic crystals of sp. gr. 7.717 at 15° ; the crystals are negative and uniaxial. Bismuth oxybromide and oxyiodide are prepared in an analogous manner, and resemble the oxychloride in their crystallographic

and optical properties. The oxybromide is colourless and has a sp. gr. 8.082 at 15°, whilst the oxyiodide is of a coppery tint and has a sp. gr. 7.922.

N. L.

Mineralogical Chemistry.

Coals, Bitumen, &c., from the Silurian of Bohemia. By C. FRIEDRICH EICHLEITER (*Chem. Centr.*, 1900, i, 624—625; from *Verh. k.k. geol. Reichsanst. Wien*, 1899, 348—362).—Several analyses are given of coals and bituminous substances from fossiliferous strata.

L. J. S.

Cerussite from the Altai. By PAVEL V. VON JEREMÉEFF (*Zeit. Kryst. Min.*, 1900, 32, 429; from *Verh. k. russ. min. Ges.*, 1899, 36, Protok., 12—15).—Twin crystals of cerussite from the Sirjanowsk mine gave, on analysis by J. A. Antipoff.

PbO.	CO ₂ .	SO ₃ .	ZnO.	CdO.	Fe ₂ O ₃ .	Al ₂ O ₃ .	H ₂ O.	Insol.	Total.
77.63	14.12	2.07	0.51	0.15	6.63	1.42	1.24	1.38	99.15

This corresponds with 87.60 per cent. PbCO₃; the iron and aluminium belong to the gangue. A crystallographic description is given.

L. J. S.

Pseudomorphs after Olivine from the Urals. By PAVEL V. VON JEREMÉEFF (*Zeit. Kryst. Min.*, 1900, 32, 430; from *Verh. k. russ. min. Ges.*, 1899, 36, Protok., 24—27).—Various pseudomorphs after olivine from different localities in the Schischimsk and Nasjamsk mountains, Urals, are described. The following analysis by Nikoléeff of the least altered crystals show them to be monticellite.

SiO ₂ .	Al ₂ O ₃ .	FeO.	CaO.	MgO.	Mn.	Loss on ignition.	Total.
36.44	0.62	2.80	32.11	25.35	trace.	1.68	99.00

The various stages in the process of alteration are suggested to be: the alteration of the olivine to serpentine, then, by the action of a solution containing an alumino-silicate, to epidote, and finally the partial alteration of the epidote to steatite and clay.

L. J. S.

Composition of Plagioclase. By W. TARASSENKO (*Zeit. Kryst. Min.*, 1900, 32, 423; from *Tagebuch X. Vers. russ. Naturf. Aertze in Kiew.*, 1898, No. 10, 379—380).—Labradorite from Selistsche, Gov. Wolinsk, was powdered and separated by a heavy liquid into six portions of sp. gr. (1) lighter than 2.647 (0.5 gram); (2) 2.647—2.669 (1.1 grams); (3) 2.669—2.675 (9 grams); (4) 2.675—2.680 (11 grams); (5) 2.680—2.710 (2.9 grams); (6) heavier than 2.710 (0.07 gram).

The four portions (2)—(5) gave on analysis the maximum and minimum results under I and II respectively.

	SiO ₂ .	Al ₂ O ₃ .	Fe ₂ O ₃ , TiO ₂ .	CaO.	Na ₂ O.	K ₂ O.	Loss at 120°.	Loss on ignition.
I.	55·33	28·44	0·42	10·32	5·37	1·26	0·11	0·36
II.	55·09	28·02	0·30	10·01	5·04	0·98	0·04	0·33

This is considered to prove that the plagioclases are not isomorphous mixtures, but compounds of the albite and anorthite molecules in definite proportions.

L. J. S.

Two New American Meteorites. By H. L. PRESTON (*Amer. J. Sci.*, 1900, [iv], 9, 283—286).—*Luis Lopez, New Mexico.*—This iron, which weighs 6903 grams, was found in 1896 near Luis Lopez, Socorro Co. It contains numerous nodules of troilite surrounded by zones of schreibersite or of a graphitic substance. The etched surface shows typical octahedral Widmanstätten figures. The structure and chemical composition (anal. I by Mariner and Hoskins) of this iron distinguish it from the five other irons (Costilla, Glorieta, El Capitan, Sacramento Mts., and Oscuro) recently found in this portion of New Mexico.

	Fe.	Ni.	Co.	Si.	P.	S.	C.	Total.	Sp. gr.
I.	91·312	8·170	0·160	trace	0·333	0·013	0·012	100·000	7·7
II.	94·734	4·620	0·180	—	0·442	0·015	0·009	100·000	7·5

Central Missouri.—All that is known of the history of this iron is that it was found in the fifties in Central Missouri. About half the mass weighs 12360 grams. It is penetrated by numerous fissures filled with a graphite-like substance, and in part by schreibersite. The etched surface is minutely pitted. Analysis by Mariner and Hoskins gave the results under II.

L. J. S.

Water from Jouhe, near Dôle (Jura). By PAUL BOURCET (*Bull. Soc. Chim.*, 1900, [iii], 23, 144—145; *J. Pharm.*, 1900, [vi], 11, 223—224).—This water is only very slightly mineralised, the principal constituents being sodium and magnesium chlorides and calcium sulphate and hydrogen carbonate, whilst, contrary to the local opinion, it contains only a trace of dissolved hydrogen sulphide; the reputation for therapeutic power that it holds does not thus appear to be justified.

W. A. D.

Physiological Chemistry.

Relative Digestibility of Certain Fats in the Human Intestine. IV. Lard Substitute ("Kunstspeisefett"). By H. LÜHRIG (*Zeit. Nahr. Genussm.*, 1900, 3, 73—87).—Comparative experiments with genuine lard, and with two mixtures of fats sent into commerce as cheap lard-substitutes, of which the first consists of two parts of tallow and three parts of cotton-seed oil, and the second of

equal parts of the first and lard, show that the coefficient of digestibility of the three preparations is identical. As in former work on the digestibility of margarine (this vol., ii, 224) lecithin and unsaponifiable substances were allowed for. The analytical constants of the fats extracted from the fæces differed widely from those of the fats consumed, and there was no means of knowing whether these fats were secretions from the walls of the intestine, or consisted of unabsorbed residues of the alimentary fats.

M. J. S.

The Proteid-sparing Action of Alcohol. By RUDOLF ROSEMAN (Pflüger's Archiv, 1900, 79, 461—483. Compare this vol., ii, 92).—Polemical. The author maintains his original contention and directs his criticisms against Offer (Wiener klin. Woch., 12, No. 41), who has disagreed with him.

W. D. H.

Parachymosin. By IVAR BANG (Pflüger's Archiv, 1900, 79, 425—441).—Rennet ferment is destroyed by long digestion with pepsin-hydrochloric acid. Some differences in the details of the time relations of this destruction suggested that in different rennet preparations there were differences in the ferment itself. Further investigation was considered to prove that there are at least two rennet ferments; one, the ordinary rennet of the calf's stomach, termed here *chymosin*, and the other, found hitherto in preparations from the stomach of pigs and men, termed *parachymosin*. The differences between the two ferments are (1) on dilution with water the proportional loss of ferment activity gives a different curve in the two cases; (2) the hastening action of calcium chloride on their activity is quantitatively different; (3) *chymosin* is destroyed at 70°, *parachymosin* at 75°; (4) *chymosin* is more resistant to alkali than *parachymosin*.

W. D. H.

Animal Juices and Tissues from the Physico-chemical Standpoint. II. Influence of the Blood Corpuscles on the Electrical Conductivity of Blood. Effect of Suspended Particles generally on Conductivity. By MAX OKER-BLOM (Pflüger's Archiv, 1900, 79, 510—533. Compare Abstr., 1900, ii, 290).—The electrical conductivity of a solution is mechanically diminished by suspended non-conducting particles, the extent of the diminution depending on the quantity and distribution of the particles, but being independent of their size (within certain limits), as well as of the absolute conductivity of the solution. The blood may be regarded as an electrolyte in which the corpuscles play the part of suspended non-conducting particles. For a given concentration of corpuscles, the ratio between the conductivity of the serum and that of the blood is constant, and independent both of the absolute conductivity of the serum and of the size of the individual corpuscles.

J. C. P.

Specific Heat of Blood. By H. BORDIER (Compt. rend., 1900, 130, 799—800).—The values of the specific heats of arterial and venous blood, given by Landois in his *Traité de Physiologie*, are respectively 1.031 and 0.892, and the author, doubting the correctness of these values, has made fresh determinations, employing the method of cooling. Blood from the ox, calf, and dog, arterial and defibrinated,

as well as blood serum and venous blood, were examined, and the means of the results are: arterial blood, 0.906; venous blood, 0.893. The mean specific heat of the whole body is probably between 0.7 and 0.8.

BERTHELOT, in a footnote to the above paper, draws attention to the fact that the author has overlooked a paper (Abstr., 1890, 274) in which he showed that the specific heat varies notably with physiological conditions, and in which he recorded many determinations of the values.
L. M. J.

Oxygen in Human Blood. By A. LOEWY (*Chem. Centr.*, 1900, i, 49; from *Centr. Physiol.*, 13, 449—453).—From investigations on the influence of lessened oxygen supply on metabolism in man, the conclusion is drawn that the process can take a normal course, even when the oxygen tension is extremely low (35, or even 30 mm.). If the alveolar oxygen tension sinks below this, 'tissue dyspnoea' sets in, because, owing to the dissociation of oxyhæmoglobin, the supply of oxygen is insufficient. New work has led to some numerical results which differ from those of Hüfner (*Arch. Anat. Physiol.*, 1890); with oxygen tension of 36—37 mm. of mercury, the oxygen saturation of hæmoglobin is 80 per cent.; at 22—23 mm. mercury, it is 58.25 per cent. Hüfner worked with crystallised hæmoglobin, the present author with fresh blood. Possibly oxygen is more firmly held in the former than in the latter case.
W. D. H.

The Sense of Smell and the most important Perfumes. By ERNST ERDMANN (*Zeit. angew. Chem.*, 1900, 103—116).—The paper, which is of a popular character, contains a list of the more important substances used as perfumes, classified as (1) aldehydes, (2) alcohols and esters, (3) ketones, (4) phenols and phenyl ethers, (5) acids and acid anhydrides, (6) nitrogenous substances, (7) hydrocarbons.
C. F. B.

Different Effect of Ions on Animal Tissues. By JACQUES LOEB (*Amer. J. Physiol.*, 1900, 3, 383—396).—A controversy exists as to whether in the heart, and also in such animals as jelly fish, the contractions are of muscular or nervous origin. In *Gonionemus*, the medusa selected for experiment, it appears certain that ordinarily—that is, in the presence of the potassium and calcium salts of the sea-water—the impulses start in the margin, and, therefore, probably in the nervous system. Above all, it is the chemical, not the histological, structure of ganglia which is important. The central portions of the medusa beat rhythmically in pure solutions of sodium chloride or bromide. Curarised skeletal muscles do the same, provided potassium and calcium are absent. The calcium, &c., is not the stimulus for rhythmical contractions in the heart and other tissues, but the sodium, calcium, and potassium must exist in definite proportions in the tissue itself. Thus, if the amount of sodium is too small, an increase produced by placing the tissue in a pure sodium chloride solution will initiate rhythm. If the amount of calcium is too small, an increase of it will start rhythmical contractions. Thus, skeletal muscle may be made to beat by increasing the amount of sodium, or by decreasing that of calcium by precipitation.

Potassium annihilates muscular activity rapidly, but ciliary action and cell division, which are considered generally to be protoplasmic actions of the same order, continue in the presence of enormous quantities of potassium salts. The riddle of contractility is therefore still unsolved if the contractile processes are the same in all these cases. The most important combination for the furtherance of various vital processes is a mixture of $5/8$ *N* potassium chloride and a small amount of $10/8$ *N* calcium chloride. In such a solution, the development of ova progresses well. That sodium salts are absent suggests that the main importance of the metals lies in the influence they have on the physical properties of protoplasm; thus, magnesium chloride will often serve as a substitute for the potassium chloride in the above mixture. The arguments in the paper are based on the theory of ionic dissociation of salts in solution.

W. D. H.

Chemistry and Physiology of the Thyroid. By AD. OSWALD (*Pflüger's Archiv*, 1900, 79, 450—460. Compare Abstr., 1899, ii, 439).—Polemical. Criticism is directed against Blum's conclusions.

W. D. H.

Elimination of Mercury by Patients treated with this Metal. By FRIEDRICH ESCHBAUM (*Chem. Centr.*, 1900, i, 628; from *Deut. med. Woch.*, 26, 52—55).—See this vol., ii, 368.

[Elimination of] Carbohydrates [in Urine]. By G. ROSENFELD (*Chem. Centr.*, 1900, i, 657—658; from *Centr. inn. Med.*, 21, 177—189).—The alcohols dulcitol, mannitol, and sorbitol resemble their respective carbohydrates, galactose, mannose, and dextrose, in regard to their capability of being eliminated in urine, and in this respect follow in the order given, the position of the first two, however, being still doubtful. Mannitol and dulcitol contribute little if anything to the formation of glycogen. Disregarding the possibility that the carbohydrates are converted into glycogen before being oxidised, then considerable quantities of these substances should occur in urine, and in fact 40 per cent. of the mannitol and 60 of the dulcitol ingested were found in human urine. These alcohols thus behave like dextrose in cases of diabetes. Pentacetylgalactose, when administered in large doses, is more easily oxidised than galactose, and also passes into the urine more readily without partaking in the production of glycogen. In this case, the pentacetylgalactose may possibly undergo an abnormal decomposition and not yield acetic acid and galactose. E. W. W.

Pharmacology of Chloretone [Acetonechloroform]. By T. B. ALDRICH and E. M. HOUGHTON (*Proc. Amer. Physiol. Soc.*, Dec., 1899; *Amer. J. Physiol.*, 1900, 3, xxvi—xxvii).—Acetonechloroform is regarded as an ideal anæsthetic for experimental purposes. The bodily functions are but little affected, and even after hypnosis lasting for days the animal recovers completely. Its action on the central nervous system is like that of other anæsthetics of the fatty series, although it differs in not depressing the circulatory system. The application of the drug to the exposed frog's heart produces slowing, but more complete contraction, much as digitalis does. It is a powerful germicide. It can be recovered from the brain substance, and although volatile

it is not eliminated from the lungs. The chlorides of the urine are increased, and small quantities of chloretone appear there also. As a surgical dressing it is satisfactory, wounds healing by first intention. Cilia and spermatozoa remain active for hours in a saturated aqueous solution.

W. D. H.

Physiological Action of Formaldehyde. By GIUSEPPE BRUNI (*Chem. Centr.*, 1900, i, 51—52; from *Ann. Farm. Chim.*, 1899, 324—345).—Formaldehyde of completely neutral reaction can be borne better than the acid commercial material by the animal organism. Administered internally, even in dilute solutions, formaldehyde causes vomiting. In a few days, with non-poisonous doses, there is hardening of the tissues. The acid solution is much more fatal to micro-organisms than the neutral. The antiseptic properties of formaldehyde are far greater than those of boric acid.

W. D. H.

[Physiological Action of] Mercury Derivatives of Aromatic Amines. By ALBERICO BENEDICENTI and ORESTE POLLEDRO (*Atti. Real. Accad. Torino*, 1900, 35, 297—318).—A series of experiments has been carried out on the toxicological action of *p*-mercuriodiphenylene-tetraethylmercuridiammonium acetate, called shortly diethyline.

Diethyline facilitates the precipitation of albumin and the coagulation of blood serum; it also hinders the putrefaction of these substances, its action in this respect resembling that of calomel. Like calomel, too, diethyline does not entirely stop the fermentative processes brought about by ptyalin and pepsin, which are, however, rendered less active; it does not impede the digestive processes of the stomach juices, but prevents putrefaction, the same action being exercised also in the intestines of the living animal. The only lower animals subjected to the action of diethyline were earthworms, which died much more quickly when immersed in a solution of the substance in olive oil than when in the pure oil; when given with food, diethyline probably acts as a vermifuge in the intestines, as in the fæces of rabbits to which it was administered numbers of small dead worms were always found.

On the vertebrates, diethyline has a slow cumulative poisoning action similar to that of other mercurial preparations; after death, the intestine shows hyperæmia, although much less intense than in acute poisoning, the liver being of a dark colour and the kidneys exhibiting small hæmorrhages. The pressure of the blood is diminished and the pulse slackened, whilst the urine shows the presence of mercury and an optically active sugar, but not of albumin.

T. H. P.

Chemistry of Vegetable Physiology and Agriculture.

Bacteria which Destroy Nitrates. By ALBERT STUTZER and R. HARTLEB (*Bied. Centr.*, 1900, 29, 126—128; from *Mitt. landw. Inst. Breslau*, 1900, Heft i, 108).—Hexoses and pentoses, like salts of

organic acids, can serve as sources of food and energy for bacteria which destroy nitrates. The non-denitrifying bacteria hitherto employed did not permanently hinder denitrification, and it is improbable that microbes exist which check the activity of those which destroy nitrates, so long as these have assimilable organic matter at their disposal under conditions of limited aëration.

It is suggested that stable manure should receive layers of calcareous material to neutralise the organic acids which act unfavourably on the bacteria present in the manure, in order, as quickly as possible, to get rid of the carbonaceous substances which are utilised by denitrifying microbes. Loss of ammonia may be hindered by covering the calcareous layers with soil or peat litter.

N. H. J. M.

Denitrification and Decomposition of Animal Matters in Soil. By CASIMIR ROGÓYSKI (*Ann. agron.*, 1900, 26, 121—140).—Soil (233 or 200 grams), both alone and with addition of sodium nitrate, horse-dung, and urine, singly and in different mixtures, was kept for different periods of several weeks in funnels under glass shades, with provision for aëration and for absorbing any ammonia which might be evolved. At the commencement and at the conclusion of the experiments, the amounts of nitrogen in different forms was determined.

The conclusion is drawn that when denitrification takes place in presence of abundance of dung, the nitric nitrogen may, according to the conditions, be eliminated in the free state, or else it may be partly or wholly transformed into insoluble nitrogenous compounds.

When urine or ammonium salts are applied to soil along with much dung or straw, the nitrogen of the urine may be liberated in the free state, or converted into an insoluble state. The insoluble substances thus produced seem to undergo nitrification readily.

The above conclusions only hold good when dung is employed in much greater amounts than occurs in practice. With amounts of dung less excessive (but still in excess of the amounts ordinarily employed), nitrates remain unchanged in the soil, and urine is nitrified. The practical conclusions drawn from the results of the German experiments on denitrification are therefore not justified (compare Dehérain, *Abstr.*, 1898, ii, 630, and 1899, ii, 800; and Warington, *ibid.*, ii, 800).

N. H. J. M.

Importance of Bacteria for the Development of Plants. By JULIUS STOKLASA (*Zeit. Zuckerind. Böhm.*, 1900, 24, 222—227).—*Brassica oleracea* was grown in enclosed vessels containing sterilised loamy sand (16 kilos.) manured with minerals and nitrate. One vessel remained sterilised in each experiment, whilst the other was inoculated with a mixture of the following soil-bacteria: *Bacillus mycoides*, *B. fluorescens liquefaciens*, *B. proteus vulgaris*, *B. subtilis*, *B. butyricus* Hueppe, *B. megatherium*, *B. uræ*, *B. mesentericus vulgatus*, and *B. coli commune*. The inoculated vessels received 5 grams of dextrose. At the conclusion of the experiment, it was found that the sterilisation of the vessels which had not been inoculated had been maintained. In the second experiment, the seed sown in the two vessels was obtained

from the corresponding plants of the first experiment. The following amounts of dry produce were obtained :

	I.		II.		III.	
	Stems, &c.	Seed.	Stems, &c.	Seed.	Stems, &c.	Seed.
Sterilised ...	11.65	1.63	8.84	0.72	9.00	0.33
Inoculated...	15.34	3.06	13.9	2.67	12.8	2.62

The results show that in absence of micro-organisms vegetation is abnormal, and that incompletely developed seed is produced.

N. H. J. M.

Influence of Light on the Respiration of Lower Fungi. By R. KOLKWITZ (*Bied. Centr.*, 1900, 29, 121—122; from *Jahrb. wiss. Bot.*, 33, 37).—In constructing a respiration apparatus, the Pettenkofer method was adopted with some modification. Compressed air free from carbon dioxide, contained in a steel cylinder, is passed over the object of the experiment, the carbon dioxide evolved being absorbed by baryta. Electric light was employed, and electricity was also employed for heating.

It was found that light increased the respiration of *Aspergillus niger*, *Penicillium*, *Micrococcus prodigiosus*, *Proteus vulg.*, *Oidium lactis*, and *Mucor spec.* to the extent of about 10 per cent.

Different investigators have obtained very divergent results, and it is thought to be necessary that the experiments should be greatly extended.

N. H. J. M.

Production of Sucrose from Dextrose in the Cell. By J. GRÜSS (*Bied. Centr.*, 1900, 29, 136; from *Ber. deut. bot. Ges.*, 1898, 16, 17—20; and *Bot. Centr.*, 1898, 75, 15).—In experiments with barley embryos from seeds kept for 12—18 hours in water, it was found that sucrose can be formed from dextrose in the cells, and that starch and cellulose can be produced from sucrose. No aldehyde group in the sucrose molecule becomes free in the production of starch and cellulose.

N. H. J. M.

Influence of Nitrogen on the Growth of Roots. By HERMANN MÜLLER-THURGAU (*Bied. Centr.*, 1900, 29, 101—103; from *Jahresber. Wädensweil.*, 6, 45).—Water-culture experiments were made with various plants, in which portions of the roots were kept immersed in nutritive solutions containing mineral food and nitrate, the rest being in similar solutions, but without nitrate.

It was found that root development was greatest in presence of nitrate, that the roots were then more branched, and that they were richer in proteids than those which were not directly fed with nitrate.

The conclusion is drawn that roots are able to produce proteids when sugar is supplied from the leaves.

N. H. J. M.

Metamorphoses and Migrations of Compounds of the Linalool Group in Plants. By EUGÈNE CHARABOT (*Bull. Soc. Chim.*, 1900, [iii], 23, 189—191).—General remarks on the results described in previous papers by the author (*Abstr.*, 1899, i, 620, 711; this

vol., i, 241; ii, 101). The changes undergone by linalool and its derivatives during development are well shown in the essential oils obtained from the leaves, flowers, and fruit of the orange (*Citrus bigaradia*). The oil from the leaves contains about 60 per cent. of acetates of linalool and geraniol, and 20—25 per cent. of the free alcohols, whilst the proportion of limonene is small, but increases as growth proceeds. In the flowering stage, the amount of limonene is considerably increased, whilst the esters and total alcohols have fallen to 15 and 50 per cent. respectively. When localised in the rind of the fruit, the proportion of limonene in the oil is still greater, but the alcohols have almost completely disappeared, the linalool having been converted into limonene and the geraniol into citral. N. L.

Influence of Active Vegetative Growth on the Formation of Thujone and Thujol. By EUGÈNE CHARABOT (*Compt. rend.*, 1900, 130, 923—926. Compare Abstr., 1899, i, 441, 620, 711, and this vol., i, 241, and ii, 101).—The author's researches on the transformation of the terpenoid constituents of the essential oils during the growth of essence yielding plants, indicate that the changes take place in two distinct stages corresponding with the principal phases of the growth of the organism. The elaboration of the alcohols and their conversion, by the elimination of water, into esters, ethers, and terpenes occurs in the green parts of the plant and corresponds with the period of active assimilation.

The second stage of the transformation involves the oxidation of the primary and secondary alcohols into aldehydes and ketones respectively, and this corresponds with that phase in the life of the plant when the respiratory function predominates over the assimilative energy.

An examination of two samples of the essential oil of *Artemisia Absinthium* indicates that, during a period of slow growth, the amount of thujol (tanacetylic) alcohol oxidised to thujone (tanacetone) is comparatively large, but that after a period of rapid assimilation the formation of the ketone does not keep pace with the elaboration of the alcohol. G. T. M.

Pure Culture of a Green Alga. Formation of Chlorophyll in the Dark. By MAXIME RADAIS (*Compt. rend.*, 1900, 130, 793—796).—The author, having succeeded in isolating the unicellular green alga *Chlorella vulgaris* of Beyerinck, cultivated specimens of the plant in total darkness in media rich in proteid matter and carbohydrate; under these conditions, the organism passes through an etiolated stage and then develops chlorophyll; when grown in the presence of light, the development proceeds in a similar manner, only the etiolated phase is shorter. Spectroscopic examination of the alcoholic and carbon disulphide extracts of the cells cultivated in the dark confirms the presence of chlorophyll and shows that it is identical with the colouring matter obtained from the plant when grown under ordinary conditions; the amount of chlorophyll produced is approximately the same in both cases. G. T. M.

Oil of Carthamus Tinctorius (Safflower Oil). By HENRY R. LE SUEUR (*J. Soc. Chem. Ind.*, 1900, 19, 104—106).—The following are

the means obtained in the determination of the constants of safflower oils: sp. gr. at 15.5° , 0.9267; saponification value, 189.83; acid figure, 6.14; iodine number, 141.29; Reichert-Meissl number, *nil*; insoluble fatty acids, 95.3; acetyl number, 16.1. Roughly speaking, the oil consists of 90 per cent. of glycerides of unsaturated acids and 10 per cent. of glycerides of saturated acids. The acids identified were stearic, palmitic, oleic, and linoleic, the last-named forming the larger portion of the oil. The oil has very good drying properties.

L. DE K.

Toxic Action of Compounds of the Alkaline-earth Metals towards the Higher Plants. By HENRI COUPIN (*Compt. rend.*, 1900, 130, 791—793).—A study of the action of calcium, strontium, and barium salts on young wheat plants shows that with soluble homologous compounds the toxic effect increases with the atomic weight; the insoluble salts of these metals are all innocuous. The soluble salts of calcium and strontium have a marked toxic action on plants, and their iodides are very poisonous; the soluble barium salts are all very injurious to plant life, the action being most intense in the case of the chlorate and iodide. The toxic equivalents of these compounds are arranged in tabular form.

G. T. M.

Assimilation by Plants in Soils containing different Amounts of Sand. By EMANUEL GROSS (*Bied. Centr.*, 1899, 29, 73—74; from *Fühling's landw. Zeit.*, 1899, 291).—Pot experiments are described in which barley and white mustard were grown in soil, and in the same soil (100 parts) mixed with 33, 100, and 300 parts of sand. No manure was added. In both cases, the yield and the amounts of nutritive constituents assimilated diminished, but this diminution was not in relation to increasing dilution of the soil with sand. As the amount of sand increased, the percentage amounts of the nutritive constituents of the soil which were assimilated also increased. In pots 1 (barley), with soil alone, and 4 (soil with 3 parts of sand), the percentage amounts utilised by the plants were: N, 27.3 and 58.5; K_2O , 37.9 and 86.8; CaO , 3.5 and 8.2; P_2O_5 , 30.2 and 72.5. It is concluded that light sandy soils require plenty of manure, not only because they are poor in nutritive substances, but because the assimilating power of plants is greater in sandy than in heavier soils.

N. H. J. M.

Relation between the Weight and the Percentage of Nitrogen in Barley Grain. By WILHELM JOHANNSEN (*Bied. Centr.*, 1900, 29, 110—112; from *Meddel. Carlsberg. Lab.*, 1899, 4, 228—313).—Ripe, completely developed grains from different ears of the same variety of barley, grown on a small experimental bed, showed great variations in the percentage of nitrogen; an average analysis of barley grain is therefore insufficient for determining the quality, from a chemical point of view, of the crop. The different ears from one plant do not as a rule vary much in composition, but occasionally they varied a good deal. This lends support to the view that the nature of an entire plant and not of a part of the plant should be

taken into account in selecting for the purpose of obtaining improved varieties.

The percentage of nitrogen generally increased with the weight of the grain ; but the different series showed considerable variations, the rise in percentage of nitrogen being sometimes great, and sometimes hardly appreciable. Ears, with large grain and low percentage of nitrogen, selected for three generations, gave, in the fourth generation, grain which was somewhat heavier, and which contained distinctly less nitrogen than the grain of previous crops.

The author considers that the doctrine of the "incompatibility of the valuable properties of cultivated plants," advocated by Schindler and von Proskowetz, is of very limited scientific value, and that, practically, it only means that certain improvements are more difficult to obtain than others.

N. H. J. M.

Fenugreek. By GIUSEPPE D'ANCONA (*Landw. Versuchs.-Stat.*, 1899, 51, 387—396. Compare Pasqualini, *Ann. Staz.-Agrar. Forli*, 1873, 1874, and 1876 ; and Jahns, *Abstr.*, 1886, 85).—Analysis of two samples of fenugreek gave the following results : Nitrogenous matter, 13·74 and 13·02 ; fat, 3·31 and 3·54 ; crude fibre, 31·75 and 29·36 ; nitrogen-free extract, 45·79 and 48·14 ; ash, 5·42 and 5·94 per cent. in the dry matter. The pure ash contained (per cent.) :

	K ₂ O.	Na ₂ O.	CaO.	MgO.	Fe ₂ O ₃ .	P ₂ O ₅ .	SO ₃ .	SiO ₂ .	Cl.
1.	19·37	7·60	30·73	1·19	4·71	8·24	4·35	21·97	1·23
2.	18·85	7·55	28·92	0·96	5·08	7·87	3·91	25·19	0·99

In composition, fenugreek resembles *Trifolium incarnatum*. Its cultivation is recommended on account of the large crops which can be got without making a great demand on the soil. There seems to be no doubt that feeding with fenugreek gives rise to an unpleasant taste both in meat and in milk, and it is suggested that the fodder might be employed for working animals. The peculiar odour of the plants observed in April and May disappears, however, at the time of cutting. The odour is attributed to the presence of an oil (Jahns, *loc. cit.*).

N. H. J. M.

Amount of Mineral Matter and Nitrogen in Sugar Beet variously manured and in different Soils. By W. SCHNEIDEWIND (*Bied. Centr.*, 1900, 29, 81—84 ; from *Blätt. Zuckerrübenbau*, 1899, 6, 145).—The results of several years' experiments showed that the amount of sugar in fresh beet generally varies, in single years, inversely with the amount of ash. When the plants take up much potash, the percentage of sugar is only lowered when the amount of ash exceeds a certain limit ; a slight increase in the amount of ash, when due to potash, will even raise the percentage of sugar.

In wet soils, the plants take up more water and mineral matter, but this does not involve greater production of organic non-saccharine matter. Except on peat land, the better kinds of beet contain very little ash compared with the varieties formerly grown ; even when heavily manured with nitrate or with dung and nitrate, the percentage of ash remains low. Application of large amounts of manure results

in a high percentage of ash in the leaves, and the production of leaf is increased by large amounts of nitrogenous manure.

In the first periods of growth, sodium nitrate is more effective than potassium nitrate, owing, it is thought, to its being more readily soluble and diffusible, and to the fact that soda is not, like potash, absorbed by the soil. At the present time, sugar-beet contains only about half as much potassium and about twice as much sodium as formerly. As regards magnesium, the amounts present in roots have not changed much, but the leaves contain a good deal less than formerly. In the case of phosphoric acid, the roots contain less than formerly, whilst in the leaves the amount has remained the same. The employment of Stassfurt salts does affect the percentage of sugar, as the chlorides are stored in the leaves; the presence of chlorides is, besides, beneficial, since they diminish the amount of organic acids to which the production of molasses is mainly due. N. H. J. M.

Use of Commercial Fertilisers for Forcing House Crops. By EDWARD H. JENKINS and W. E. BRITTON (*21st Annual Rep. Agr. Exper. Stat. Connecticut* for 1897, 278—308. Compare Abstr., 1899, ii, 511).—*Tomatoes.* A mixture of coal ashes and peat with chemical manures gave greater yields than a rich compost of peat and manure. The greatest yield was obtained after application of sodium nitrate, 6·4 lb., dissolved bone black, 1 lb., and ammonium chloride, 2·4 lb. per 100 square feet. In presence of large amounts of soluble plant food in ashes and peat, the root system is much less extensive than in the case of plants growing in compost.

The experiments with carnations and radishes (*loc. cit.*) were also continued. N. H. J. M.

Vegetation Experiments with Sugar Beet. By H. WILFARTH and G. WIMMER (*Zeit. Ver. Deut. Zucker-Ind.*, 1900, 173—194).—The cultivation of sugar beet involves greater difficulties than is the case with cereals, potatoes, tobacco, &c., the quality as well as the yield being affected by unsuitable conditions. Variations in quality occur chiefly in the percentage of sugar and in the quotient; and not only the total nitrogen, but especially the amount of amides, has to be considered.

Excess or deficiency of water, nitrogen, and potassium are the conditions which most affect the beet-crop; and large amounts of nitrogen are only permissible when other conditions are satisfactory. The tendency to rot is shown to be connected with an alkaline secretion, due to the separation of the bases of the nitrate. To overcome this difficulty, gypsum is applied in conjunction with potassium nitrate, and the amount of humus is increased by addition of peat. Even when calcium nitrate is employed, lime may be liberated more quickly than it can be converted into carbonate. In dry seasons, abundance of potassium seems to compensate for deficiency of water.

Amides were determined by boiling the pulp (50 grams) with water (250—300 c.c.) and hydrochloric acid of sp. gr. 1·124 (6 c.c.) for half an hour, and distilling with *magnesia usta* into standard sulphuric acid.

Paraffin is added to prevent frothing. The small amounts of ammonia produced from proteids, &c., are not of practical importance.

N. H. J. M.

Does Nitrogenous Manure injure succeeding Crops when applied to Seed Beet? By H. WILFARTH (*Zeit. Ver. Deut. Zucker-Ind.*, 1900, 58—65).—The results of the author's experiments indicate that heavy applications of nitrogenous manure to sugar-beet grown for seed have no injurious effect on subsequent crops grown from the seed so obtained. The conclusion accords with what has been observed in practice (compare Rimpau, *Oesterr. Zeit. Zuckerind.*, 19, 615; Marek, *ibid.*, 1885, 768; Strohmer, Briem, and Stift, *ibid.*, 1892, 21, 244; and 1895, 279, 788, and Abstr., 1896, ii, 538; and Drechsler, *J. Landw.*, 1877, 117).

N. H. J. M.

Analytical Chemistry.

Gas Absorption Apparatus. By ARMAND GAUTIER (*Bull. Soc. Chim.*, 1900, [iii], 23, 141—144).—The apparatus consists of two bulbs, each of about 10 c.c. capacity, connected together by a straight, vertical tube 10—12 cm. long, reaching nearly to the bottom of the lower bulb, and also by a long spiral wound round the vertical tube. The gas first enters the lower bulb and then ascends the spiral, where it is broken up into a series of small bubbles and brought into intimate contact with the absorbing liquid, which subsequently descends into the lower bulb by means of the straight, vertical tube. The apparatus is compact, readily weighed with accuracy, and very efficient.

N. L.

Estimation of Iodic Acid in Sodium Nitrate. By R. AUZENAT (*Chem. Centr.*, 1900, i, 571; from *Mon. sci.*, [iv], 14, i, 72).—Both nitrates and iodates liberate iodine from potassium iodide on addition of sulphuric acid, but only the latter do so when acetic acid is used. A colorimetric estimation is based on this fact.

M. J. S.

Estimation of Sulphites and Thiosulphates in the presence of each other. By GEORG LUNGE and D. SEGALLER (*J. Soc. Chem. Ind.*, 1900, 19, 221—223).—The authors state that the unsatisfactory results obtained by Richardson and Akroyd with Lunge and Smith's process for the estimation of mixed sulphites and thiosulphates by means of standard iodine and potassium permanganate (*ibid.*, 1883, 2, 463) were caused by their not exactly following the directions laid down in the original paper. The process has been tried again with results quite as satisfactory as those given by Richardson and Akroyd's own process (*Abstr.*, 1898, ii, 91).

In Lunge and Smith's process, there are only two titrations to be made, whilst in Richardson and Akroyd's process there are three; the former method is consequently the more expeditious.

L. DE K.

Estimation of Phosphoric Acid soluble in 2 per cent. Citric Acid Solution. By ALEXANDER HERZFELD (*Zeit. Ver. Deut. Zucker-Ind.*, 1900, 77—78).—The abnormal result previously described (this vol., ii, 243) was due to the want of full details of the method employed by the German Experiment Stations.

The method, which has been published by Wagner, is as follows: a half-litre flask containing alcohol (5 c.c.) and the basic slag (5 grams) is filled to the mark with 2 per cent. citric acid solution (at 17.5°), placed at once in a rotary apparatus (turning 30—40 times a minute) for half an hour, and then immediately filtered.

(1) 50 c.c. of the filtrate are treated with molybdate solution (100 c.c.), placed for 10—15 minutes in a water-bath heated at 60° or 90—95°. When cold, the precipitate is collected, washed with 1 per cent. nitric acid, and dissolved in about 100 c.c. of cold 2 per cent. ammonia. The solution is precipitated with 15 c.c. of magnesia mixture, being well stirred, and left for about 2 hours.

(2) 50 c.c. of the extract is at once treated with 50 c.c. of magnesia mixture containing citrate, and stirred, or violently agitated, for 30 minutes. The precipitate is filtered within half an hour.

N. H. J. M.

Volumetric Estimation of Boric Acid. By BERNHARD FISCHER (*Zeit. Unters. Nahr. Genussm.*, 1900, 3, 17—21).—To obtain accurate results by Jörgensen's method, the following precautions should be observed. The boric acid should be in combination with potassium or sodium. Organic matter should be destroyed by incineration, which may be carried to complete fusion if a little alkali carbonate is added. The aqueous solution of the fused mass is coloured by methyl-orange, and dilute sulphuric acid is added in the cold until the mixture is distinctly red. A few drops more acid are added, and the liquid is boiled for a moment to expel carbon dioxide. The liquid, which has become yellow on heating, is again completely cooled, when the red colour should return. It is then accurately neutralised, by first adding sodium hydroxide until yellow, and then *N/2* sulphuric acid until the transition tint is obtained. Glycerol and phenolphthalein are added, and the acidity is estimated with *N/2* soda. When the red colour is obtained, it is well to add a further quantity of glycerol, and if no more soda is then required than that necessary for the acidity of the glycerol itself (which should always be estimated and allowed for), the titration may be regarded as finished. With careful observations of the indicator tints the results are very close, and with such substances as margarine (saponified without using alcohol) are of almost theoretical accuracy; but the method is inapplicable to meat (compare Beythien and Hempel, this vol., ii, 313), since phosphates disturb the results seriously.

M. J. S.

Colorimetric Method for the Estimation of Silica in Mineral Waters. By ROBERTO SALVADORI and G. PELLINI (*Gazzetta*, 1900, 30, i, 191—194).—The estimation of silica by Jolles and Neurat's method (*Abstr.*, 1898, ii, 455) gives good results with the water of Bagnoli (*Abstr.*, 1899, ii, 771), but with waters containing a large proportion of salts, especially halogenated compounds, discordant

numbers are obtained. The presence of phosphoric or arsenic acid has no disturbing influence on the determination. The yellow colour with molybdic acid solution is just visible with a solution containing 0.003 gram of silica per litre, which must be regarded as the limit of sensitiveness of the method.

T. H. P.

Mechanical Analysis of Soils. Separation of Clay and Sand. By GIUSEPPE SCARLATA (*Chem. Centr.*, 1900, i, 571; from *Staz. sperim. agrar. ital.*, 32, 634).—About 5 grams of the soil are placed in a thin beaker, of 500 c.c. capacity, furnished at one side with a stop-cock syphon, and at the other with a stop-cock tube by which water can be admitted. The soil is acidified with hydrochloric acid, and water is added until it reaches to 2 cm. from the edge of the beaker, and while keeping the level constant, a slow stream of water is passed through the vessel, which meanwhile is gently warmed. When the supernatant liquid is perfectly clear, the flow of water should be stopped, and the contents of the beaker boiled; if the separation is complete, the liquid will remain clear. The results agree well with those obtained with Schloesing's apparatus.

M. J. S.

Detection of Mercury in Urine. By M. HOEHNEL (*Chem. Centr.*, 1900, i, 627—628; from *Pharm. Zeit.*, 45, 126).—1 litre of urine is concentrated on the water-bath to 250 c.c., 3—4 grams of pure potassium cyanide are added, and the whole heated for half an hour at 60—70°. Into the brown filtrate 2 or 3 strips of carefully cleaned copper foil are introduced, and the whole is left for 2 hours at 60—70°; the strips of copper are then taken out, washed with water and alcohol, and exposed for half an hour to the air. If the urine contained mercury, this will form the well-known deposit on the copper, which may be further verified in the usual manner.

L. DE K.

Clinical Estimation of Mercury in Urine. Elimination of Mercury in Patients treated with this Metal. By FRIEDRICH ESCHBAUM (*Chem. Centr.*, 1900, i, 628; from *Deut. med. Woch.*, 26, 52—55).—The process is briefly as follows. The urine is boiled with some dextrose, and a sufficient amount of aqueous sodium hydroxide is added to precipitate the phosphates. After pouring off the clear, supernatant liquid, the precipitate is dissolved in hydrochloric acid and then heated at 45—60° with copper gauze. This, after being duly washed with alkali, water, and alcohol, is dried for half an hour in the air and then heated in a glass tube; the mercury which condenses on the cold sides of the tube is removed by introducing a weighed piece of silver foil with which it instantly amalgamates. The increase in weight represents the mercury; by way of a check, the silver may be heated and the mercury found by the loss in weight.

The urine of patients treated with Werler's ointment, which contains 10 per cent. of colloidal mercury, showed, after 48 hours, distinct traces of mercury; this could still be detected for 6 weeks after the cure.

L. DE K.

Electrolytic Estimation of Lead in the Sulphate and Chromate. Application to the Analysis of Lead Glass and Lead Chromates. By CH. MARIE (*Compt. rend.*, 1900, 130, 1032—1033).—The lead sulphate or chromate is dissolved in a mix-

ture of nitric acid and ammonium nitrate, and the solution electrolysed at 60—70° in the usual manner. Lead glass is subjected to a preliminary treatment with sulphuric and hydrofluoric acids in order to convert the bases into sulphates. N. L.

Analysis of Copper. By JOHN CLARK (*J. Soc. Chem. Ind.*, 1900, 19, 27—28).—The solution, which must contain free hydrochloric acid, is mixed with excess of potassium iodide and then with sufficient sodium sulphite to remove the free iodine. If the solution should contain free nitric or sulphuric acid, it must first be rendered alkaline with sodium carbonate, and afterwards be cleared by means of hydrochloric acid. The cuprous iodide, derived from at least 10 grams of the metal to be tested, is thrown on a filter and washed, first with dilute hydrochloric acid, and then with cold water. The filtrate is boiled until the sulphur dioxide is expelled, and then mixed with excess of ammonia or aqueous sodium hydroxide, which should not produce a precipitate; ammonium or sodium sulphide is added to precipitate the last traces of copper, and also any lead, bismuth, &c.; arsenic, tin, and antimony are not precipitated. By adding excess of hydrochloric acid and passing hydrogen sulphide, the arsenic, tin, and antimony are precipitated as sulphides, and may be separated by boiling in a distilling flask with strong hydrochloric acid, whereby the arsenic sulphide is decomposed and volatilised (*Trans.*, 1892, 61, 424); the arsenic may then be recovered from the distillate by means of hydrogen sulphide. The solution left in the flask, and containing the antimony and tin, is then boiled with steel turnings, which throw down the antimony as metal, and reduce the tin to the stannous state; this is precipitated as sulphide, and finally converted, as usual, into oxide and weighed. The antimony and the undissolved steel are dissolved in hydrochloric acid and potassium chlorate, precipitated with hydrogen sulphide, and the antimony finally weighed as sulphide.

The metals which have been precipitated with ammonium sulphide in the alkaline tartrate solution may be dissolved in hydrochloric acid and a little potassium chlorate, precipitated with hydrogen sulphide, and then redissolved by means of hydrochloric acid and potassium chlorate. The bismuth and copper are precipitated by means of steel turnings (see this vol., ii, 371), converted into sulphides, dissolved in nitric acid, and the bismuth thrown down with ammonium carbonate, and weighed as oxide. To the filtrate from the bismuth and copper, excess of sodium acetate is added, and any lead (unless this has already been removed before precipitating the copper with potassium iodide) is precipitated with sulphuric acid and weighed as sulphate. Iron, nickel, zinc, &c., are estimated in the usual way.

The process previously referred to for separating arsenic, antimony, and tin will be found very useful in qualitative analysis. The mixed sulphides are introduced into a small flask, mixed with about 20 c.c. of strong hydrochloric acid, and distilled into a test-tube containing water; if arsenic is present, a yellow precipitate, due to arsenic trisulphide, makes its appearance. The residual liquid is filtered, if necessary, boiled with steel (not iron) turnings to precipitate the antimony, and the filtrate tested for stannous tin with mercuric

chloride. The antimony is mechanically removed from the steel, then dissolved in hydrochloric acid and potassium chlorate, and its solution divided into two parts; in one of these, the antimony is tested for with hydrogen sulphide, and to the other the test with zinc on platinum foil is applied.

L. DE K.

Estimation of Copper in Cyanide Solutions. By J. E. CLENNELL (*J. Soc. Chem. Ind.*, 1900, 19, 14—16).—10 to 50 c.c. of the solution to be tested, which must be perfectly clear, are placed in a 100 c.c. flask, and *N*/10 sulphuric acid is added from a burette with continual shaking, until the turbidity formed ceases to disappear, but leaves the liquid slightly milky. After carefully reading the burette, a further quantity (*A*) of the acid is added, more than sufficient to precipitate the whole of the copper. The flask is now filled up to the mark with water and thoroughly shaken, when the precipitate will generally settle rapidly in a flocculent condition. 50 c.c. of the supernatant liquid are now filtered and titrated with *N*/10 solution of sodium carbonate, a single drop of methyl-orange (1 : 400) serving as indicator. The strength of the sodium carbonate solution must be accurately determined with reference to the sulphuric acid used in the first stage of the test. The number of c.c. of sodium carbonate used, multiplied by 2, gives approximately the equivalent of the excess of sulphuric acid beyond that required to precipitate the copper.

Let *B* represent the number of c.c. of sodium carbonate used for 50 c.c. of the filtrate, and *C* the number of c.c. of sulphuric acid equivalent to 2*B*, then *A* - *C* represents the number of c.c. of sulphuric acid equivalent to the copper present.

L. DE K.

[Analysis of] Molybdenum Sulphides. By MARCEL GUICHARD (*Bull. Soc. Chim.*, 1900, [iii], 23, 147—156).—The preparation of molybdenum disulphide and sesquisulphide has been already described (this vol., ii, 144 and 211); in the present paper an account of the analytical methods employed is also given. The sulphides are decomposed by heating with nitric acid or by fusion with potassium nitrate and sodium carbonate, and the nitric acid removed by evaporation with hydrochloric acid; the sulphuric and molybdic acids thus formed are finally weighed as the barium and lead salts respectively. The molybdenum alone may be estimated by igniting the sulphide, with or without previous treatment with nitric acid, at a temperature below redness, and weighing the residue of molybdenum trioxide. Molybdenite may be conveniently heated to bright redness in a current of oxygen when molybdenum trioxide sublimes, whilst the iron and silica are found in the residue.

N. L.

Phosphotungstic Acid as a Reagent for Potassium. By EMIL WÖRNER (*Chem. Centr.*, 1900, i, 517; from *Ber. Deut. pharm. Ges.*, 10, 4).—Neutral or acid solutions of potassium and ammonium salts give a white precipitate with phosphotungstic acid. Slight warming favours, alcohol hinders, the precipitation. To distinguish potassium from ammonium, the precipitate may be boiled with sodium hydroxide, and after acidifying with hydrochloric acid, the reagent added afresh. A fraction of a milligram of potassium chloride gives the reaction distinctly.

M. J. S.

Separation of Bismuth from Lead. By JOHN CLARK (*J. Soc. Chem. Ind.*, 1900, 19, 26—27).—The solution containing the two metals, which should be in the form of chlorides, is boiled with steel turnings which rapidly bring down the bismuth; care must be taken to have a slight excess of the steel, as otherwise a portion of the bismuth will redissolve.

The bismuth and the undissolved steel are washed with water, dissolved in hydrochloric acid with the aid of potassium chlorate, and the bismuth is then precipitated as sulphide; this, after being thoroughly washed free from iron, is dissolved in nitric acid and precipitated with ammonium carbonate. The bismuth carbonate is then converted into oxide and weighed. L. DE K.

Detection of Minute Quantities of Gold in Ores. By THEODOR DÖRING (*Chem. Centr.*, 1900, i, 516—517; from *Berg.-Hüttenm.*, 59, 49).—Otto has shown that a white, infusible ash of paper acquires a rose-red to purple coloration if the paper has been soaked in a solution which leaves metallic gold when ignited, and has suggested the extraction of ores with either tincture of iodine or bromine water for the purpose. The author finds the most efficient solvents to be a mixture of ether and bromine, or one of equal volumes of bromine and aqueous hydrobromic acid of sp. gr. 1.49. An aqueous solution of iodine in hydriodic acid also dissolves gold readily. Otto's method will detect 0.75 gram of gold in a ton of ore. M. J. S.

New Microchemical Reaction of Palladium. By M. E. POZZI-ESCOT and H. C. COUQUET (*Compt. rend.*, 1900, 130, 1073).—If, after the addition of potassium nitrite to a solution of palladium chloride, an excess of an alkali hydroxide or ammonia is immediately added, the temperature of the mixture being kept low, a palladium potassium nitrite is formed which is deposited as slightly yellow, rhombohedral crystals. This microchemical reaction is a characteristic and delicate test for palladium salts. H. R. LE S.

Estimation of Iridium in Alloys of the Noble Metals. By W. MIETZSCHKE (*Chem. Centr.*, 1900, i, 572—573; from *Berg.-Hüttenm. Zeit.*, 59, 61).—To extract the iridium from an alloy containing gold, silver, and platinum, with or without oxidisable metals, four quantities of 0.25 gram are taken, cupelled, fused with silver (quartated), and two of the buttons boiled with nitric acid, two with sulphuric acid. The gold is submitted to quartation a second time, and then boiled with nitric acid, by which means silver and platinum are removed. Part of the iridium will be found floating in the silver solution, which should be filtered to recover it. The iridium-gold is dissolved in aqua regia, when most of the iridium will be left undissolved. The gold is thrown down by ferrous sulphate, and the remainder of the iridium is obtained by evaporating the filtrate.

If the iridium-gold alloy is free from other metals, it may be fused in a crucible in a muffle, and kept at a high temperature for 1—2 hours. The whole of the iridium will deposit on the crucible. After pouring off the fused gold, litharge and a reducing flux with a cover

of common salt are fused in the crucible; the lead button is cupelled with much silver and the silver alloy examined for iridium. M. J. S.

Method and Apparatus for Incinerating Vegetable and Animal Substances. By A. E. SHUTTLEWORTH (*Bied. Centr.*, 1900, 29, 117—121; from *J. Landw.*, 1899, 47, 173; and *Inaug.-Diss., Göttingen*, 1899. Compare Shuttleworth and Tollens, this vol., ii, 111).—Fusion of ash, and the consequent increase in the amount of ash constituents insoluble in hydrochloric acid, is avoided by addition of calcium acetate (compare Wackenroder, *Arch. Pharm.*, [ii], 53, 9). Pure calcium acetate (free from magnesia) is prepared by dissolving marble in hydrochloric acid, and after separating the iron, precipitating as oxalate. This is well washed and afterwards ignited, and the lime dissolved in boiling dilute acetic acid. A 1 per cent. solution is convenient, 20 c.c. being employed for 5—6 grams of oat straw, sufficient water being added to enable the acetate to be properly distributed. The amount of lime corresponding with the acetate employed is deducted from the weight of the ash.

The apparatus for incinerating consists of a deep dish, several covers and caps for covering the dish, and an air-pipe which passes through the cover and cap into the dish. The whole is made of platinum and weighs about 70 grams; a sketch is given in the original paper.

The method enables ashes to be prepared in less than four hours, without fusion or volatilisation of chlorides. The carbon dioxide in the ash can be determined in the apparatus. N. H. J. M.

Estimation of Naphthalene in Coal Gas. By HAROLD G. COLMAN and JAMES F. SMITH (*J. Soc. Chem. Ind.*, 1900, 19, 128—130).—The process employed is based on that adopted by Küster (*Abstr.*, 1894, ii, 333) for the separation of naphthalene from other solid hydrocarbons which do not form stable compounds with picric acid. The gas to be tested is passed by means of a specially constructed apparatus through a series of absorption bottles filled with a standardised solution of picric acid; this forms an insoluble compound with naphthalene, and the excess of picric acid is then titrated with decinormal barium hydroxide, using lacmoid as indicator. L. DE K.

Volumetric Estimation of Iodoform in Dressings. By MARTIN LEHMANN (*Chem. Centr.*, 1900, 19, 693; from *Pharm. Zeit.*, 45).—10 grams of the material are treated in a stoppered bottle with 100 grams of "spiritus æthereus" at 15—20° for 30 minutes with frequent shaking. 10 grams of the solution are mixed in an Erlenmeyer flask with 15—20 drops of fuming nitric acid, an excess of *N*/10 silver nitrate is added, and the whole heated on the water-bath until the silver iodide has deposited and the supernatant liquid is colourless. When cold, the liquid is diluted with 125—140 c.c. of water, and the excess of silver titrated according to Volhard's directions. L. DE K.

Some Analyses of Modern "Dry" Champagne. By OTTO ROSENHEIM and PHILIP SCHIDROWITZ (*Analyst*, 1900, 25, 6—8).—A table is given showing the analysis of 13 representative samples of modern "dry" French champagne.

Carbon dioxide was estimated by regulating the flow of gas by means of a hollow corkscrew with an accurately-fitting tap, drying the gas by means of sulphuric acid, and absorbing it in a weighed soda-lime tube, the last traces of gas being removed from the liquid by heating in a water-bath and transmitting a current of pure air.

The other figures were obtained by working according to the instructions laid down in the German Wine Law, 1896, and include: specific gravity at 15°, rotation in 20 cm. tube, alcohol by weight, free acidity calculated as tartaric acid, volatile acidity calculated as acetic acid, extract, ash, total tartaric acid, sugar as invert sugar, glycerol, extract (sugar - 1), and the relation of reduced extract and ash.

L. DE K.

Isolation of Pentose and Methylpentose [from Urine]. By PETER BERGELL and FERDINAND BLUMENTHAL (*Chem. Centr.*, 1900, i, 518; from *Arch. Anat. Phys.*, 1900, 155).—Several litres of urine are feebly acidified with sulphuric acid and concentrated on the water-bath to 300 c.c. The liquid is then decolorised with animal charcoal and made alkaline with barium hydroxide. After filtration, double the volume of alcohol is added, whereon the barium compound, $(C_5H_{10}O_3)_2 + BaO$, is precipitated, if at least 1.5 per cent. of pentose is present. If less is present, dextrose should be added, the barium compound of which will carry down the pentose. Methylpentose does not yield a barium compound of sparing solubility in alcohol.

M. J. S.

Estimation of Sugar in Glycerin-soaps. By FRANZ FREYER (*Chem. Centr.*, 1900, i, 693—694; from *Oesterr. Chem. Zeit.*, 3, 25—26).—16.28 grams of the soap are dissolved in 50—100 c.c. of water on the water-bath, a slight excess of 10 per cent. solution of barium chloride is added, and the whole diluted to 260 c.c., the extra 10 c.c. being supposed to compensate for the volume occupied by the barium soap.

The filtrate is then tested, as usual, for sucrose, by means of the polariscope before and after inversion; or Fehling's solution may be used.

L. DE K.

Automatic Apparatus for the Estimation of Pentosans. By VL. STANĚK (*Zeit. Zuckerind. Böhm.*, 24, 227—230).—In the Chalmot-Tollens method of estimating pentosans by distilling with 12 per cent. hydrochloric acid, after each 30 c.c. of distillate has collected, 30 c.c. of fresh acid are added to the distilling flask. To avoid the constant attention required by the ordinary method of carrying out this process, an apparatus has been devised by which the necessary additions of fresh acid are made automatically. An electrical indicator comes into action when the total distillate reaches any desired volume.

T. H. P.

Estimation of Formaldehyde. By JULES WOLFF (*Zeit. Unters. Nahr. Genussm.*, 1900, 3, 87—93).—For concentrated formaldehyde solutions, Blank and Finkenbeiner's method (*Abstr.*, 1899, ii, 188) is employed with slight modifications. A quantity of the substance containing about 0.4 gram of formaldehyde is treated with 10 c.c. of

3*N* sodium hydroxide, and 15 c.c. of hydrogen peroxide of 12 volumes per cent. previously diluted to 50 c.c. with water. A stronger peroxide solution is to be avoided. The reaction is complete in 10—15 minutes. Any acidity in either the hydrogen peroxide or the formaldehyde solution is estimated and allowed for. For solutions containing only traces of formaldehyde, a colorimetric process, based on Trillat's reaction (Abstr., 1899, ii, 130) may be used. A measured quantity of the solution is placed in a stoppered 50 c.c. flask, and mixed with 1 c.c. of glacial acetic acid and 1 c.c. of dimethylaniline; the flask is shaken for 2 minutes and then heated for 4—5 hours at 60°, keeping closely stoppered. Comparative estimations with solutions of known strength, and one without formaldehyde, are started and carried on simultaneously. Each mixture is then transferred to a small distillation flask, and after making feebly alkaline with sodium hydroxide (using phenolphthalein as indicator), 30 c.c. are distilled from it to remove excess of dimethylaniline. The residue is then acidified with acetic acid, and all the solutions are made up to the same volume. Equal quantities are now placed in test-tubes of equal diameter and mixed with lead peroxide suspended in water (4 grams per litre), adding sufficient to develop the blue colour to its fullest extent. The final comparisons are made after heating the contents of the tubes to boiling. The limit to the detection of formaldehyde by this reaction is 0.56 mg. in 50 c.c. If much alcohol is present, the liquid must be diluted five-fold with water, and the mixture with dimethylaniline must not be warmed, but should be left for 20 hours at 15—20°. The comparison solutions should be made up with the addition of the same amount of pure alcohol as in the quantity of substance taken.

M. J. S.

Testing of Acetone. By JAMES T. CONROY (*J. Soc. Chem. Ind.*, 1900, 19, 206—209).—According to the specification issued by the Government, acetone should show the following properties: (1) It should have a sp. gr. of 0.800 at 60° F. Mixed with distilled water, it must show no turbidity, and must leave no residue on evaporation at 212° F. On distillation, 80 per cent. by volume should distil over below 138° F. The liquid left in the distilling flask should not contain any ingredient foreign to crude acetone. (2) 1 c.c. of a solution of potassium permanganate (1:1000) added to 100 c.c. of the sample should retain its distinctive colour for not less than 30 minutes. (3) The sample should not show more than 0.005 per cent. of acetic acid when tested as follows: 50 c.c. are diluted with 50 c.c. of distilled water, mixed with 2 c.c. of solution of phenolphthalein (1:1000 proof spirit) and then titrated with *N*/100 soda.

Commenting on these tests, the author calls attention to the influence exercised by the temperature on the permanganate test; a definite temperature should therefore be fixed. When estimating the acidity, great care should be taken to use distilled water completely free from carbon dioxide, and blowing the pipette should be avoided. It is also stated that samples which are to be submitted to these tests should not be exposed to light, as the effect will be prejudicial.

L. DE K.

Examination of Violet Preparations for Ionone. By R. SCHMIDT (*Zeit. angew. Chem.*, 1900, 189—192).—A crude oil is first isolated, in the case of an alcoholic solution by diluting it with water and extracting it with ether; in the case of a pomade by distilling it with steam and extracting the distillate with ether. The crude oil left on evaporation of the ether must itself be employed for estimations; for qualitative tests, it may be distilled under reduced pressure, and the fraction boiling at 125—135° under 12 mm. pressure utilised.

As a preliminary experiment, a little of the oil may be mixed with an acetic acid solution of *p*-bromophenylhydrazine. The crude hydrazones of α - and β -ionone melt at 138—140° and 110—115° respectively; the pure substances melt at 143° and 118°.

In order to isolate the ketones, the crude oil is shaken with a slightly acid solution of sodium *p*-hydrazinebenzenesulphonate, then made slightly alkaline, and shaken with ether and so much ammonium sulphate as will cause a separation into three layers, the ethereal layer being removed and renewed frequently. The two aqueous layers are together treated with phthalic anhydride, and distilled with steam; the distillate is extracted with ether, and the ethereal solution distilled. A loss of 10 per cent. is inevitable. For qualitative tests, the crude ketones may be distilled, and the fraction boiling at 125—135° under 12 mm. pressure employed.

In order to separate and detect the α - and β -ionone, the crude ketones are boiled with a little alcohol and an aqueous solution of sodium sulphite and hydrogen sulphite. The solution is purified by extraction with ether, and then distilled, when β -ionone passes over, and may be identified by means of its semicarbazone, which melts at 148°. Sodium hydroxide is added to the residue, and the distillation continued, when α -ionone passes over; it may be identified by means of its *p*-bromophenylhydrazone.

The method last described permits of the detection of a small amount of β -ionone in the presence of much α -ionone. In order to detect a little α -ionone in presence of much β -ionone, the semicarbazones are prepared under such conditions that all of the α - and some of the β -semicarbazone remain dissolved, whilst much of the latter separates. The alcoholic mother liquor is warmed with dilute sulphuric acid and then extracted with ether; the oil extracted is converted into the crude *p*-bromophenylhydrazone, by repeated crystallisation of which the pure α -derivative is obtained.

Exact details of the processes are given in the paper. C. F. B.

Estimation of Propionic and Butyric Acids in Acetic Acid. By MAX MUSPRATT (*J. Soc. Chem. Ind.*, 1900, 19, 204—206).—If the acetic acid is known to contain either propionic or butyric acid (usually *isobutyric* acid), the amount may be estimated indirectly by first titrating the mixture with pure sodium hydroxide and afterwards weighing the mixed anhydrous sodium salts.

If both propionic and *isobutyric* acids are suspected, the mixture is neutralised within about 5 per cent., and distilled to dryness. A convenient quantity of the distillate is then carefully neutralised with sodium carbonate, and evaporated in a platinum dish. From the weight

of the anhydrous salt and the acidity of the distillate, the results are calculated as acetate and isobutyrate. Sufficient absolute alcohol is now added to dissolve the butyrates, and after evaporating the solution, the residue is weighed, ignited, and titrated. The isobutyrate calculated from this should agree with that found previously, unless propionic acid is present.

If the results do not agree, the presence of propionic acid is assured. The author recommends for its detection the process recommended by Linnemann, which is based on the insolubility of basic lead propionate in boiling water. As, however, the basic lead salt of *n*-butyric acid is also very insoluble, *n*-butyric acid interferes with the test.

L. DE K.

Separation of Oleic Acid from other Fatty Acids. By JULIUS LEWKOWITSCH (*Analyst*, 1900, 25, 64—66).—The process recommended by Twitchell, based on the insolubility of sulphonated oleic acid in light petroleum (Abstr., 1899, ii, 69), and that recommended by Farnsteiner, based on the insolubility of barium oleate in a mixture of benzene and alcohol (Abstr., 1899, ii, 705), are found to be untrustworthy.

L. DE K.

Free Fatty Acid in Olive Oil. By RUSSELL W. MOORE (*J. Soc. Chem. Ind.*, 1900, 19, 223).—7.05 grams of the oil are introduced into a 4 oz. bottle by means of an accurate pipette, 50 c.c. of a 10 per cent. sodium chloride solution are added, and the free acids titrated with $N/4$ alkali, using phenolphthalein as indicator, and thoroughly shaking the mixture after each addition of alkali.

The number of c.c. of alkali used represent the percentage of free (oleic) acid in the sample. The process can also be used for solid fats by employing hot sodium chloride solution.

L. DE K.

Determination of the Iodine Value. By J. J. A. WIJS (*Analyst*, 1900, 25, 31—33. Compare Lewkowitsch, this vol., ii, 323).—A controversy with Lewkowitsch on some minor points in the determination of the iodine value by means of a solution of iodine monochloride in acetic acid.

The author agrees that allyl alcohol is not a substance specially suitable for deciding the respective values of the different methods for determining iodine values. Lewkowitsch's objection to the use of acetic acid of 95 instead of 99 per cent. strength is overruled.

L. DE K.

The Iodine Value of Oils. By ARTHUR MARSHALL (*J. Soc. Chem. Ind.*, 1900, 19, 213—215).—A solution of iodine monochloride in pure carbon tetrachloride is recommended instead of the ordinary Hübl solution, as it may be obtained perfectly free from any moisture, thus preventing secondary actions.

L. DE K.

Relation between the Specific Gravity, Fat, and Solids not Fat, in Milk. By NORMAN LEONARD (*Analyst*, 1900, 25, 67—69).—This is a slight modification of the formula proposed by Richmond in 1895: $T = 0.25$, $G + 1.2$, $F + 0.14$, in which T represents the total solids, G the excess of the sp. gr. over 1000, and F the fat.

The new formula given is $F=0.796$, $T-0.210$, $G+0.30$.

Both formulæ give, however, practically the same results, and it is only in the case of rich milks that the difference may amount to more than 0.1 per cent.

L. DE K.

Adulteration of Cotton-seed Oil with Maize Oil. By GIULIO MORPURGO and ALB. GÖTZL (*Chem. Centr.*, 1900, 1, 694—695; from *Oesterr. Chem. Zeit.*, 3, 53—54).—The two oils are chiefly distinguished by their iodine numbers, and by the melting points of their fatty acids. The iodine numbers of cotton-seed oil and maize oil are respectively 111—113 and 130.2—151.4; the melting points of the fatty acids, 36—37° and 18—20°. Notwithstanding this, 25 per cent. of maize oil may be added to cotton-seed oil without its presence being readily detected.

L. DE K.

Detection of Margarine in Cheese. By G. FASCETTI and F. GHIGI (*Chem. Centr.*, 1900, i, 573—574; from *Staz. speriment. agrar. ital.*, 32, 593).—The solvent employed to extract the fat from cheese must be one which does not alter it in any respect; the cheese should therefore first be extracted with water at 30—35°, and then the fat dissolved out with ether. Leffmann and Beam's modification of the Reichert-Meissl method avoids certain sources of error and saves time. In genuine cheese, the volatile acid number exceeds 18, margarine cheese gives values below 15, and generally below 6. As shown by Windisch, the proportion of free acids of both natural and artificial cheese-fats is but little affected by the ordinary conditions of ripening. The refraction values at 35° of genuine cheese lie below 47.5°, those of margarine cheese above 48°, but the latter fall during ripening. Complete analyses of four margarine cheeses are given in the original paper.

M. J. S.

Some Properties of Rosin, with Special Reference to the Analysis of the Fatty Matter of Soap. By ALFRED SMETHAM and F. ROBERTSON DODD (*J. Soc. Chem. Ind.*, 1900, 19, 101—103).—It is shown that the iodine number of rosin is much reduced by the saponification process, although the saponification and acid values are not much affected thereby; this is of some importance when dealing with saponified rosins in the analysis of the mixed fatty acids of soap. But the fact that the iodine number is so high, that it much depends on the process employed (Hübl's, Wijs's), and that it is after all very uncertain, renders its direct application to soap analysis of doubtful value.

L. DE K.

Detection of "Saccharin" in Articles of Food. By R. TRUCHON (*Chem. Centr.*, 1900, i, 691; from *Ann. Chim. anal. appl.*, 5, 48—49).—The following modification of Schmitt's process is used in the Paris official laboratory: 200 c.c. of the liquid to be tested are acidified with phosphoric acid and shaken three times in succession with 35—40 c.c. of a mixture of ether and light petroleum; the ethereal liquid is washed with water and then evaporated in a platinum dish. 5—6 drops of aqueous sodium hydroxide are added to the residue and the whole gently fused over a small flame of a Bunsen burner until no more gas bubbles are noticed. The fused mass is dissolved in water,

acidified with sulphuric acid, and extracted twice in succession with 30 c.c. of benzene; this is allowed to evaporate in a porcelain dish and the residue is then tested for salicylic acid with ferric chloride.

L. DE K.

Technical Analysis of Liquorice Pastes. By M. TRUBECK (*J. Amer. Chem. Soc.*, 1900, 22, 19—21).—Hager's process, in which ammonia and alcohol are used, gives quite erroneous results when liquorice paste contains added glucose, as the percentage of glycyrrhizin so found may then be as much as 10 per cent. in excess of the truth. The following process is recommended: 2 grams of the sample are well stirred with 5 c.c. of warm water, and 20 c.c. of alcohol are added; the liquid is filtered, and the residue washed with dilute alcohol (1:4) until the washings are colourless. The residue is then dried at 105° and weighed; it represents the gummy matter, starch, &c. The filtrate is evaporated, finally in a small beaker, to 1 or 1.5 c.c., then dissolved in 2 c.c. of glacial acetic acid and mixed with 30 c.c. of absolute alcohol. The crude glycyrrhizic acid is then collected on a weighed filter, washed with absolute alcohol, dried at 105° for 3 hours and weighed, then incinerated, finally heating over the blow-pipe, and any ash so obtained weighed, and 0.7 of its weight deducted from the weight of the acid.

The filtrate from the glycyrrhizin is evaporated, the residue is moistened a few times with water, and finally dried for 3 hours at 105° and weighed; this represents saccharin matters, tannins, resins, &c.

The estimation of water, ash, matters soluble in cold water, and saccharin matters is effected in the usual manner.

L. DE K.

Colour Reaction for Tyrosine. By GEORGES DENIGÈS (*Compt. rend.*, 1900, 130, 583—585).—2 c.c. of sulphuric acid are very carefully mixed with 3 to 5 drops of a solution of aldehyde in twice its volume of alcohol of 90°, care being taken that the liquid remains colourless. A few drops of a solution of tyrosine are then added, and the liquid rapidly acquires a gooseberry-red colour, the intensity of which is proportional, within certain limits, to the quantity of tyrosine present. In this way, it is possible to recognise tyrosine in a solution containing only 1 part in 10,000, if 0.1 c.c. of the solution is taken. By using solutions of tyrosine of known strength, the quantity of tyrosine in the liquid under examination may be rapidly estimated colorimetrically. The reagent is not affected by proteids and peptones, but is affected by certain phenolic compounds.

A solution of commercial formalin in 50 vols. of sulphuric acid gives with tyrosine a brown coloration which eventually becomes reddish. This colour changes to green if the liquid is mixed with twice its volume of glacial acetic acid and boiled.

C. H. B.

Detection of Phenetidine in Urine. By G. EDLEFSEN (*Chem. Centr.*, 1900, i, 573; from *Centr. inn. Med.*, 21, 2).—According to Müller (*Therap. Monatsh.*, 12, 357), phenetidine can be detected in the urine after doses of phenacetine by diazotising and adding an alkaline solution of α -naphthol. The author finds that Müller's alkaline ether extract of the urine does not always give the reaction, the phenetidine

being present as an ethyl sulphonate, which requires to be boiled with hydrochloric acid before it will give Müller's indonaphthol reaction. The cooled liquid is shaken with 1—2 drops of a 1 per cent. nitrite solution. One-half of the mixture is treated with a drop or two of 4—5 per cent. alcoholic α -naphthol and then made alkaline. In presence of phenetidine, a pure red coloration is produced, which becomes a deep cherry-red on acidifying with hydrochloric acid. The other half is treated with 1 to 2 c.c. of a 3 per cent. phenol solution and sodium hydroxide; a yellow coloration is obtained, passing into pale red on acidifying. Müller's method is only suitable when a larger amount of phenetidine is present. M. J. S.

Reactions of Antipyrine, Tolpyrpyrine, Aminoantipyrine and Pyramidone. By PAUL HOFFMANN (*Chem. Centr.*, 1900, i, 519; from *Arch. intern. Pharm. Therap.*, 1899, 171).—The reactions of these compounds are described with auric chloride, ferric chloride, the Brouardel-Boutmy reagent, silver nitrate, potassium dichromate, Wagner's reagent, nitrous acid, bromine water, and blood solution with hydrogen peroxide. Aminoantipyrine and pyramidone being more oxidisable than antipyrine and tolpyrpyrine, reduce auric chloride in the cold, the two latter only on boiling. The two former give also blue or violet colours with nitrous acid, bromine water, blood, ferric chloride, and the Brouardel-Boutmy reagent, whilst the two latter either give no reaction or one of another colour. Aminoantipyrine and pyramidone may be distinguished by the last three of these reagents.

M. J. S.

Coffee Extracts, their Composition and Analysis. By CRESACE G. MOOR and MARTIN PRIEST (*Analyst*, 1899, 24, 281—283).—The percentage of extract, ash, total nitrogen, and caffeine is given for 10 samples of commercial coffee extracts, including 4 samples which also contained chicory extract. The figures representing the percentage of caffeine are in fair agreement with those obtained by the analytical sanitary commission of the *Lancet* in 1894.

Attention is called to the difficulty of making a proper division of the sample into three parts for the purpose of official analysis, as most of the caffeine may be at the bottom of the bottle as a sparingly soluble tannate; if the sample is warmed, this will completely redissolve.

L. DE K.

Estimation of the Alkaloids of the Leaves of Datura Stramonium, Hyoscyamus Niger, and Atropa Belladonna. By ERNST SCHMIDT (*Chem. Centr.*, 1900, i, 376—377; from *Apoth. Zeit.*, 15, 13—14).—10 grams of the dried and powdered leaves are shaken with 90 grams of ether and 30 grams of chloroform, 10 c.c. of a 10 per cent. solution of sodium hydroxide added, and the whole frequently shaken for 3 hours; 10 c.c. of water are then added, and after an hour 60 grams of the clear chloroform-ether solution (= 5 grams of the leaves) are filtered. This is distilled to about one-half, and the residue shaken in a separating funnel with 10 c.c. *N*/100 hydrochloric acid. This is collected, and the chloroform is washed thrice with 10 c.c. of water. The acid solution is filtered,

the washings being also passed through the same filter, which is finally washed until the total filtrate measures 100 c.c. The liquid is covered with 1 cm. layer of ether, 5 drops of alcoholic solution of iodoeosin (1:500) added, and the excess of acid titrated with *N*/100 potassium hydroxide until the aqueous layer turns pale rose-red. A blank experiment is then made in the same manner, and the amount of alkaloid is calculated from the hydrochloric acid used for its neutralisation.

L. DE K.

Detection of Nicotine. By IWAN SCHINDELMEISER (*Chem. Centr.*, 1900, i, 67; from *Pharm. Centralhalle*, 40, 703).—When treated with a drop of 30 per cent. formaldehyde (free from formic acid) and a drop of concentrated nitric acid, nicotine gives a rose-red solution. It is better to leave the mixture of nicotine and formaldehyde for some hours before adding the nitric acid. As little as 0.5 mg. of nicotine will show the reaction, which is not interfered with by coniine, piperidine, trimethylamine, pyridine, quinoline, picoline, or aniline. The reaction was not obtained with extracts of decomposing horse-flesh, or the intestines of animals poisoned by tin, mercury, or arsenic, extracted by the Stas-Otto process. Too much formaldehyde must not be added, nor must the mixture be warmed, as in either case explosive decomposition will occur.

M. J. S.

Ullmann's Tests for Tanning Materials and Basic Colours used in Dyeing. By ADOLF HEINEMANN (*Chem. Zeit.*, 1900, 24, 58).—The colorimetric tests by means of basic colours, proposed by Ullmann, are stated to give untrustworthy results, as they do not sufficiently distinguish between tannic acid and gallic acid, which is of no use as a mordant.

L. DE K.

Distinguishing Between Hops and Quassia. By ALFRED C. CHAPMAN (*Analyst*, 1900, 25, 35—37).—The process is based on the fact that hop bitter yields valeric acid when oxidised with an alkaline solution of potassium permanganate, whilst quassia and chiretta do not yield any; camomile extract, however, behaves in a similar manner to hops.

The beverage to be tested, beer, for instance, is evaporated to dryness with some sand; the mass is then dried in an air-bath, powdered and extracted with ether. The ether is filtered into a flask, and after recovering the bulk by distillation, the last traces are driven off by warming the flask on the water-bath. A solution containing 40 grams of potassium permanganate and 10 grams of potassium hydroxide per litre is now added in small portions until the permanganate ceases to be readily reduced; warming and shaking promote the action. The excess of permanganate is then reduced by adding a sufficiency of oxalic acid, and the filtered liquid evaporated in a glass dish. If now the residue is moistened with dilute sulphuric acid, the odour of valeric acid will at once become apparent if hop bitter is present; in the case of quassia, a faint odour of acetic acid will be noticed.

L. DE K.

General and Physical Chemistry.

Spectra of Metals in the Electric Arc. V. Spectrum of Vanadium. By H. HASSELBERG (*K. sv. vet. Akad. Handl.*, 1900, 32, 2).—After careful comparison with the spectra of iron, titanium, chromium, manganese, cobalt, and nickel, the author gives a full list of the lines he regards as belonging to vanadium. His results agree in the main with those of Rowland. J. C. P.

Transparency of Aluminium to Radiations from Radium. By HENRI BECQUEREL (*Compt. rend.*, 1900, 130, 1154—1157. Compare Abstr., 1899, ii, 393; this vol., ii, 126, 182).—A series of experiments which confirm the author's previous statements that when radiations from radium fall on an aluminium screen, some are absorbed, some diffused, and others transmitted; the last have properties identical with those of the incident radiations. Of the secondary radiations which are also emitted, some are deviated by the magnetic field, whereas others are not (compare Villard, *Compt. rend.*, 1900, 130, 1012). H. R. LE S.

Radiations from Radium. By P. VILLARD (*Compt. rend.*, 1900, 130, 1178—1179).—When the radiations from radium fall on a glass plate 1 cm. in thickness, or on a sheet of lead 0.3 mm. in thickness, practically all the radiations which are deviated by a magnetic field are absorbed, whereas the others (those not so deviated) are transmitted almost completely. H. R. LE S.

Theory of the Latent Image. By EUGEN ENGLISH (*Chem. Centr.*, 1900, i, 706; from *Arch. wiss. Phot.*, 2, 50—52).—According to Schaum, the small lateral extension of the darkening compared with its depth points to the capability of development being due to the action of chemically active rays, and not to that of silver germs. This fact, however, must not be quoted against the contact theory, as is done by Eder. The subhaloid theory is to be rejected because, according to it, the undeveloped fixed image should be twice as strong as the developed fixed image. It appears that an appreciable part of the silver bromide is altered in the light, and thus prepared for development. If this can be proved, both the silver germ and subhaloid theories must be given up (compare Abegg; Luther, this vol., ii, 253). J. C. P.

Reversibility of Voltaic Cells. By T. SIDNEY MOORE (*Phil. Mag.*, 1900, [v], 49, 491—496).—Experiments were made to test the reversibility of the following voltaic cells; copper and zinc in solutions of their sulphates and of their chlorides, copper and cadmium in solutions of sulphates or chlorides, and the Clark cell. The experimental method is described and the results indicate that all the cells examined were reversible, the slight differences in the E.M.F.'s observed being within the limits of experimental errors. L. M. J.

Alleged Identity of Red and Yellow Mercuric Oxides. II. By ERNST COHEN (*Proc. K. Akad. Wetensch. Amsterdam*, 1900, 2, 458—460. Compare this vol., ii, 184).—The E.M.F. of the mercuric

oxide cell previously described increases from 0.685 millivolt at 25° to 0.773 millivolt at 35°, so that the temperature coefficient is 0.0088 millivolt. When this value is introduced in the equation

$$\pi = E/n\epsilon_0 + T.d\pi/dT,$$

E , the heat of transformation of the yellow into the red oxide, is calculated to be -89.4 cal. Varet found the heat of reaction of the red oxide with hydrocyanic acid to be 31550 cal., whilst Berthelot found 31600 cal. for the heat of reaction of the yellow oxide with the same acid. The difference of -50 cal. is of the same order as the value calculated above.

J. C. P.

Electrical Conductivity of Liquid Ammonia Solutions. By EDWARD C. FRANKLIN and CHARLES A. KRAUS (*Amer. Chem. J.*, 1900, 23, 277—313. Compare Abstr., 1899, ii, 202, 208, 284).—The authors regard the work of Cady (Abstr., 1898, ii, 203) and Goodwin and Thompson (*Phys. Rev.*, 1899, 8, 38) as being of a merely qualitative nature, and accordingly describe a complicated apparatus in which liquid ammonia can be purified, and isolated for a length of time. Numerous compounds have been used as solutes, and the conductivity of the resulting solutions has been determined by Kohlrausch's method. The molecular conductivity at infinite dilution for solutions of binary salts in ammonia at -38° ranges from 290—340 Kohlrausch units; a much greater value than that for the corresponding aqueous solutions at 18°, probably owing to the greater ionic velocities in ammonia solutions. The dissociation of binary salts, however, is, as a rule, less than in aqueous solutions, and Ostwald's dilution law holds approximately for solutions of these salts in ammonia. Silver iodide is dissociated in ammonia, although to a less extent than other binary salts; mercuric cyanide and silver cyanide both give conducting solutions, but the molecular conductivity of the former falls slightly, that of the latter rises slightly, with dilution. The only ternary salt fully examined, strontium nitrate, has a high molecular conductivity, and, as in aqueous solution, it approaches its maximum more slowly than the binary salts. Many nitro-compounds are good conductors when dissolved in ammonia; so are generally acid and basic amides. These latter are regarded as acids and bases, derived from ammonia in the same way as oxygen acids and bases are derived from water; this analogy is borne out by the chemical behaviour of ammonia solutions of the amides and by their action on indicators. In agreement with Cady, the authors find that ammonia solutions of the alkali metals conduct electricity without polarisation at the electrodes. The molecular conductivity of these solutions changes but slightly with the concentration; the temperature coefficient is positive.

J. C. P.

Electrolysis of Sodium Chloride. By C. G. L. WOLF (*J. Physical Chem.*, 1900, 4, 200—206).—The author describes a form of U-tube, fitted with a stirrer, which he used for the electrolysis of sodium chloride and the examinations of the gases liberated at each electrode. The solution of sodium chloride contained about 300 grams per litre, with 1.8 grams of potassium chromate added, and the current employed was about 1 ampere. The percentage inefficiency

at the cathode was but slight, being seldom over 1 per cent.; but at the anode it varied more, being usually about 20 per cent., and during the experiment of 7·4 ampere hours, 12·7 per cent. of the sodium chloride had been oxidised to chlorate. It was found that variations of temperature had a great effect on the efficiency, and that efficient stirring is necessary.

L. M. J.

Application of Faraday's Law to the Electrolysis of Fused Salts. By A. HELFENSTEIN (*Zeit. anorg. Chem.*, 1900, 23, 255—316. Compare Lorenz, this vol., ii, 333).—The author has electrolysed the chlorides of lead, zinc, tin, cadmium, and silver, and lead bromide and iodide, and has studied the influence of varying conditions on the current yield. Neither in a V-tube, nor in any simple apparatus which allows direct contact of the anode and cathode liquids, can a decomposition be effected equal to that required by Faraday's law. Rise of temperature, decrease of current strength, decrease of the distance between the electrodes, and prolongation of the electrolysis have the effect of diminishing the current yield; in the case of lead iodide, however, the yield increases for a certain interval, 600—800°, with rise of temperature, probably owing to the formation of per-iodide. The chief cause of the imperfect yields obtained is the solubility of the metal in its fused halogen compounds, and a consequent diffusion to the anode and to the surface of the electrolyte, where the metal is oxidised or goes off as vapour. Special experiments, in which a regulus of the metal was kept in contact with its fused halogen compound, showed that the solubility and rate of diffusion increase with rise of temperature. The diffusion of the halogen from the anode, although of less account than the diffusion of the metal from the cathode, is also responsible for a diminution of the yield; this influence of the halogen increases from chlorine to iodine.

An approximately theoretical yield is obtained when the disturbing factors enumerated above are removed. The anode and cathode are separated from each other, either by being enclosed in tubes with lateral openings, or by the interposition of a diaphragm. As is to be expected, the enclosing of the cathode is much more essential than the enclosing of the anode. Further, the electrolyte is allowed to solidify on the surface, so as to prevent diffusion of metallic vapour into the atmosphere, and the temperature is kept as low as possible—just above the melting point of the salt. With these precautions, a yield is obtained which is independent of temperature, current strength, and duration of the experiment.

J. C. P.

Electrolytic Conductivity of Saturated Solutions. By HARRY M. DAWSON and P. WILLIAMS (*Zeit. Elektrochem.*, 1899, 6, 141).—Apparatus is described in which the saturated solution may be filtered and transferred to the vessel in which the conductivity is to be measured without change of temperature and without exposure to the air.

The conductivity of supersaturated solutions of some readily soluble salts, such as magnesium sulphate, potassium carbonate, calcium chloride, decreases as the concentration increases. In the

case of salts having a transition point, this may be determined by making a series of determinations of the conductivities of solutions saturated at different temperatures. When the results are plotted in a diagram, curves are obtained which intersect at the transition temperature. The method is especially applicable to salts which are not readily soluble in water. The transition temperature of the hydrates of thorium sulphate, $\text{Th}(\text{SO}_4)_2 \cdot 9\text{H}_2\text{O}$ and $\text{Th}(\text{SO}_4)_2 \cdot 4\text{H}_2\text{O}$, was found in this way to be 48° . Determinations with the dilatometer and tensimeter gave respectively 46.5° and 47.8° . T. E.

Reducing Action of Electrolytically Deposited Metals. By A. BINZ and A. HAGENBACH (*Zeit. Elektrochem.*, 1899, 6, 261—271).—When indigotin is suspended (a) in a solution of sodium hydroxide, (b) in a solution of zinc oxide in sodium hydroxide, and the two liquids are placed in the cathode compartments of two electrolytic cells with zinc cathodes through which the same current is passed, then the indigotin in solution (b) is more rapidly reduced than that in solution (a). The deposition of zinc at the cathode would thus appear to exercise a more vigorous reducing action than the evolution of hydrogen. Indigotin is not a very suitable substance, however, since it is insoluble in the liquids used. Subsequent experiments were made with solutions of diamine-pure-blue, Ponceau R, and patent blue N. The influence of the cathode metal was first investigated. The solution was placed in the cathode compartments of two cells which differed only in the nature of the cathode metal, and through which the same current was passed. The colouring matters were dissolved in solutions of potassium hydroxide or of potassium or sodium acetate. The metals used were copper, platinum, zinc, and mercury, and in the case of the latter no amalgam was formed, the alkali metal being re-dissolved as fast as it separated. Practically no difference was found in the rate of reduction with the different cathodes. By using a concentrated solution of pure potassium hydroxide, an amalgam of potassium is obtained at a mercury cathode which is acted on very slowly by the solution. With a dilute solution of potassium hydroxide, the potassium is dissolved out of the amalgam much more rapidly. By using a concentrated and a dilute solution of potassium hydroxide, it is therefore possible to have evolution of hydrogen in one cell, and formation of amalgam in another. In this way, it is shown that, when hydrogen is evolved, the reduction of the colouring matters takes place very much more slowly than when an amalgam is produced. These experiments point to the alkali metal being the real reducing agent, and not the hydrogen liberated by the action of the metal on water. To test this further, zinc is caused to separate at a mercury cathode from a saturated solution of zinc oxide in sodium hydroxide in one cell, and hydrogen to separate from a solution of sodium hydroxide at a copper electrode in the other, both cells containing the same colouring matter. No hydrogen is evolved by the contact of the zinc amalgam with the solution, so that any reduction which occurs must be due to zinc. As a matter of fact, it is found that the reduction always takes place more rapidly in the cell with the zinc than in that in which the equivalent quantity of hydrogen is liberated. The

authors conclude that many cases of supposed reduction by nascent hydrogen are really cases of direct reduction by a metal. T. E.

Theory of Solution Pressure. By S. ROSLINGTON MILNER (*Phil. Mag.*, 1900, [v], 49, 417—423).—The author regards the proof given by Nernst for the expression representing the difference of potential between a metal and the solution of an electrolyte containing the metal in the ion state to be unsatisfactory, as the possibility of actually carrying out the individual process of the cycle is not apparent. He therefore deduces similar expressions by a slightly different method of consideration which is free from these objections. When the value of the solution pressure is excessively large, as in the case of zinc (10^9 atmos.), the author considers it to be due to the inapplicability of the gas laws over such a great range of pressure, and in this case P is merely a constant, such that $RT \log P$ represents the value of $\int v dp$ of the ions between unit pressure and the actual solution pressure. L. M. J.

Determination of some Coefficients of Magnetic Susceptibility. By STEFAN MEYER (*Ann. Phys.*, 1900, [iv], 1, 664—667. Compare this vol., ii, 7).—The magnetic susceptibility of solutions of vanadium chloride is independent of the dissociation, and the molecular susceptibility of this compound is found to be 1.25×10^{-6} . This value stands in a simple relation to those obtained for the iron group [$V : Ni : Cr : Fe' : Co : Fe : Mn = \frac{1}{2} : 2 : 2\frac{1}{2} : 3 : 4 : 5 : 6$].

A higher value is found for the susceptibility of gadolinium oxide than that previously obtained; it is supposed, on the ground of spectroscopic investigation, that the old preparation contained more or less of a strongly magnetic element. From samarium sulphate, a value is found for the atomic susceptibility agreeing well with earlier determinations. J. C. P.

Atomic and Molecular Magnetism. By STEFAN MEYER (*Ann. Phys.*, 1900, [iv], 1, 668—672. Compare this vol., ii, 7).—The results previously recorded are supplemented by an investigation of the magnetic susceptibility of copper compounds. The fundamental difference in the magnetic behaviour of cupric and cuprous salts, suggested by Wiedemann, is not borne out by the experiments; cupric and cuprous sulphides are about equally diamagnetic.

The molecular volume and molecular magnetism are compared with the sum of the atomic volumes and atomic magnetisms respectively, and it is seen that when contraction takes place in the formation of the compound, the molecular magnetism is increased; when an increase of volume takes place, the diamagnetic character becomes more marked. Hence it is permissible to calculate the atomic magnetism of an element from the molecular magnetism of its compounds only when the molecular volume of the compound is equal to the sum of the atomic volumes.

The author points out the advantages of his method of determining magnetic susceptibility over that of du Bois and Liebknecht (this vol., ii, 127). J. C. P.

Deduction of Reaction Isotherms and Isochors for Systems involving Dissociation. By KIKUNAYE IKEDA (*Zeit. physikal. Chem.*, 1900, **33**, 287—294).—A theoretical paper, not suitable for abstraction. J. C. P.

Overflowing Thermocalorimeter. By GUSTAVE MASSOL (*Compt. rend.*, 1900, **130**, 1126—1128).—Regnault's thermocalorimeter can only be used for small ranges of temperature below 40—50°. The instrument may be employed at temperatures of 250° and 300° if concentrated sulphuric acid is employed as the expanding liquid instead of alcohol; it also becomes possible to work through considerable ranges of temperature by adopting an overflow principle as in Walferdin's maximum weight thermometer. By means of this form of thermocalorimeter, the author has determined the specific heats of salt solutions at temperatures near their boiling and freezing points.

G. T. M.

Critical Temperatures of some Organic Sulphur Compounds. By L. FERRETTO (*Gazzetta*, 1900, **30**, i, 296—302).—Using Altschul's method and apparatus (*Abstr.*, 1893, ii, 446), the author has determined the following critical temperatures: ethyl mercaptan, 228°; methyl sulphide, 231·2°; ethyl sulphide, 284·67°; methyl ethyl sulphide, 259·66°; *iso*amyl mercaptan, 334° (?). The following compounds show decomposition below their critical temperatures, which were hence determined in ethereal solution, Pawlewski's formula for mixtures being employed: *iso*amyl mercaptan, 320·92°; *iso*amyl sulphide, 391·25°; allyl sulphide, 380·38°; ethyl disulphide, 368·93°. The following are the differences between the critical temperatures and the boiling points at ordinary pressures: ethyl mercaptan, 191·8°; methyl sulphide, 193·9°; ethyl sulphide, 191·77°; ethyl methyl sulphide, 193·76°; *iso*amyl mercaptan, 200·92°; *iso*amyl sulphide, 176·25°; allyl sulphide, 241·0°; ethyl disulphide, 216·13°. Thus Pawlewski's law, that for comparable substances there is a constant difference between the critical temperature and the boiling point, holds well amongst the first group of four of the above compounds, whilst for *iso*amyl mercaptan and *iso*amyl sulphide, the critical temperatures of which were determined in ether, the agreement with the law is less good. Guldberg's law of the constancy of the ratio between the absolute critical and boiling points is obeyed well by all the above compounds except *iso*amyl sulphide, the value for which, 1·38, differs considerably from Guldberg's number (1·55). The difference between the critical temperatures of two homologous compounds of the above series is roughly proportional to the difference in composition. The following table shows the differences between the critical temperatures of these sulphur derivatives and those of the corresponding oxygen compounds:

				Difference.
EtSH	228°	EtOH	244°	— 16
C ₅ H ₁₁ ·SH	320·92	C ₅ H ₁₁ ·OH	306·6	— 14·32
SMe ₂	231·2	Me ₂ O	129·6	+ 101·6
SEt ₂	284·67	Et ₂ O	191	+ 93·67
SMeEt	259·66	OMeEt	167·7	+ 91·96
S ₂ Et ₂	372·76	Et ₂ O ₂	191	+ 181·76

Thus in the ethers, the substitution of an atom of sulphur for one of oxygen raises the critical temperature by about 90° to 100° , whilst with the alcohols, the difference is much smaller and in the opposite direction.

T. H. P.

Heats of Combustion and Formation of Iodine Compounds. By MARCELLIN P. E. BERTHELOT (*Compt. rend.*, 1900, 130, 1094—1101).—Iodine compounds are completely burnt in the calorimetric bomb by the use of compressed oxygen and a priming of gun-cotton, the whole of the halogen being liberated. The following thermochemical constants are recorded :

	Molecular heat of combustion.		Molecular heat of formation.
	Constant vol.	Constant pressure.	
Methyl iodide.....	196.1 Cal.	196.5 Cal.	+ 1.3 Cal.
Methylene „	178.1	178.4	– 14.9
Iodoform	161.8	161.9	– 33.1
Ethyl iodide	355.4	356.0	– 24.0
<i>n</i> -Propyl „	512.3	514.3	+ 10.2
<i>iso</i> -Propyl „	507.4	509.1	+ 15.0
Allyl „	476.85	478.33	– 22.9
Iodobenzene	770.0	770.7	– 32.3
<i>o</i> -Iodobenzoic acid	769.4	769.6	+ 63.1
<i>o</i> -Iodosalicylic „	706.5	706.4	+ 126.3
Diiodosalicylic „	700.2	699.9	+ 98.3
Ethylene iodide.....	324.3	324.9	+ 1.7
Tetriodoethylene	261.6	261.6	– 73.0
Iodopyrrole (iodole), C_4HNI_4 ...	503.3	503.1	– 91.4

The substitution of solid iodine for gaseous hydrogen in methane is always attended by an absorption of heat, the values for the introduction of successive atoms of the halogen being -17.6 , -17.0 , and -18.2 Cal. The difference between the heats of formation of allyl and propyl iodides has the same value as that for the corresponding alcohols, namely, -33.1 Cal. The heat absorbed by the substitution of iodine for hydrogen in benzene is -28.2 Cal., whilst in the case of benzoic acid it is -31.1 Cal. The introduction of the first atom of iodine into salicylic acid is accompanied by a thermal change of -12.5 Cal., whilst that of the second produces an absorption of -28.0 Cal. These results explain the non-formation of aromatic iodo-derivatives by direct substitution. The addition of iodine (1 mol.) to ethylene produces a heat change of 16.3 Cal., whilst the substitution of the four hydrogen atoms of this olefine by iodine is accompanied by an absorption of heat, namely, -58.4 Cal. The thermal effect of introducing four iodine atoms into the pyrrole ring is -73.4 Cal.

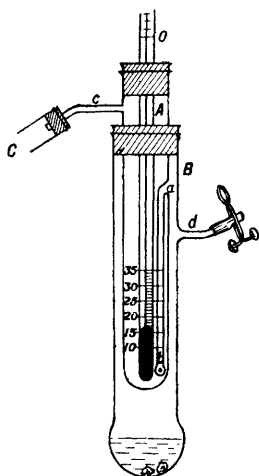
G. T. M.

Apparatus for determining Molecular Weights by the Boiling Point Method. By HERBERT N. MCCOY (*Amer. Chem. J.*, 23, 353—360).—In applying Walker and Lumsden's modification of Landsberger's method (see Abstr., 1898, ii, 283 ; Trans., 1898, 73, 502),

the author has combined the functions of the jacket and the boiling flask, as shown in the accompanying sketch.

Suitable quantities of the pure solvent are introduced into the outer tube, *B*, and the inner tube, *A*. The solvent in *B* is boiled, and if the side tube, *d*, be closed, the vapour passes through the tube *a*, which has five small perforations at its lower extremity, *b*, into the solvent in *A*. The latter is thus raised to its boiling point, and the excess vapour passes through the tube *c* to a Liebig's condenser. When the constant temperature of the boiling solvent has been ascertained, the side tube, *d*, is opened, and the boiling interrupted until a weighed quantity of the solute has been introduced into the inner tube; as in Walker and Lumsden's apparatus, the inner tube is graduated, so that the volume of the solution can be read off. Test experiments, in which various substances were dissolved in alcohol, benzene, ether, or water, gave very satisfactory results.

J. C. P.



A Manostat. By A. SMITS (*Zeit. physikal Chem.*, 1900, 33, 39—46).—An apparatus has been devised to secure a steady pressure during boiling point experiments, the deviations not exceeding 1 mm. of

water. The space in which the pressure is to be kept constant is connected (1) with the shorter limb of a mercury manometer, (2) with a suction pump. If the latter is working to begin with, then the mercury in the shorter limb of the manometer rises, and at a certain point touches a copper rod, thereby completing a circuit containing an electromagnet; the first circuit is so combined with a second circuit with a second electromagnet that the suction pump is shut off, and is connected again only when the mercury has fallen below the point of the copper rod. The pressure in such an apparatus increases very slightly with a rise of the external temperature, and is independent of the variations of the atmospheric pressure.

J. C. P.

Disturbing Influences at the Critical Point of Pure Liquids and Mixtures. By RUDOLF VON HIRSCH (*Ann. Phys.*, 1900, [iv], 1, 655—663).—The influence of gravity on the critical phenomena is discussed. It is also pointed out that the appearance or disappearance of the meniscus lags behind the temperature, and experiments with ether show that the extent of this lag depends very much on the rate of change of temperature. As the mean of a number of determinations with different tubes, 194.7° is given as the critical temperature of ether.

The author considers that the above influences are sufficient to account for many of the anomalies observed at the critical point, and that there is no need to replace van der Waals' theory by newer ones.

J. C. P.

Determination of the Decrease in the Vapour Tension of Solutions by means of the determination of the Increase in the Boiling Point. By A. SMITS (*Proc. K. Akad. Wetensch. Amsterdam*, 1900, 2, 469—477).—The boiling vessels used were made of silver, and could be connected with the manostat devised by the author (see this vol., ii, 388). Enamel grains and silver tetrahedra were employed to induce regular boiling, and the condensed vapour flowed back through a tube with outlets turned away from the thermometer. With a steady pressure, the boiling point of water remained constant to 0.002° ; but it was noticed that a 1 cm. vertical displacement of the thermometer caused a difference of 0.01 — 0.03° in its indications.

Two such silver vessels, *A* and *B*, containing distilled water, were connected with the manostat, and the temperature of boiling recorded. A weighed quantity of solute was introduced into *A*, and the pressure was adjusted so that the boiling point of the solution was the same as that of the pure water under the original pressure. The thermometer immersed in the boiling water in *B* had now fallen, and the difference between the readings of the two thermometers corresponded with the decrease of vapour tension due to the dissolved substance. The results of the investigation are to be communicated later. J. C. P.

Theory of Vapour Pressure. By R. GAHL (*Zeit. physikal. Chem.*, 1900, 33, 178—214).—A method is described for the measurement of the partial pressures of electrolytes dissolved in water, and especially applicable to very small pressures; it consists essentially in the aspiration of a known volume of air through (1) the solution and (2) a flask of perfectly pure water, the partial pressure being estimated from the increase of conductivity of the water in this flask. As is evident, many precautions are necessary to ensure accuracy with a method of this nature, and of these a full account is given. The author investigates theoretically, from the thermodynamical basis, the relations between partial pressure and cryoscopic depression, and calculates the former, in the case of hydrogen chloride, from Roloff's freezing point determinations (*Abstr.*, 1896, ii, 291). The values so obtained are compared with direct determinations by the above method, the agreement being satisfactory, as, for example, 6.74 per cent. acid, found 0.0094 mm. mercury, calc. 0.0094 ; 3.5 per cent., found 0.00117 mm., calc. 0.00116 . From the values of the partial pressure of hydrochloric acid, the decomposition tension in salts of organic bases may be determined in the case of the insoluble salts of insoluble bases by finding the strength of the acid with which the salt is in equilibrium. If a solution of ammonium chloride be boiled, owing to dissociation and the greater partial pressure of ammonia, the distillate is alkaline and the residue acid, but the author finds that air passed over solid ammonium chloride causes no increase of conductivity in the water; the salt is hence not dissociated, and possesses but a very small vapour pressure. Equations similar to those previously deduced also hold for mixtures of two or three components, and the author discusses the cases of sulphuric acid hydrates and of hydrated crystals. The partial

pressure of sulphuric acid in solution could not be determined by this method, however, owing to the fact that the acid sufficiently concentrated to give a measurable pressure showed also a partial dissociation with formation of sulphur dioxide. L. M. J.

Liquefaction of Gaseous Mixtures of Carbon Dioxide and Sulphur Dioxide. By F. CAUBET (*Compt. rend.*, 1900, 130, 828—829).—The experiments previously recorded (this vol., ii, 191) are extended to mixtures of carbon dioxide and sulphur dioxide, eight different mixtures being examined, and the critical line obtained. Retrograde condensation is obtained at all compositions, and, for the most favourable mixtures, is observed between wide limits of temperature and pressure, namely, 7° and 30 atmos., whilst the ratio of the maximum volume of the liquid to the total volume is also great, reaching 0.2. L. M. J.

Relative Rates of Effusion of Argon, Helium, and some other Gases. By FREDERICK G. DONNAN (*Phil. Mag.*, 1900, [v], 49, 423—446).—The rate of effusion, that is, efflux through a small hole in a thin-walled partition, is theoretically considered; assuming that viscosity effects are eliminated, that the ideal gas laws hold, that the efflux is adiabatic, and that the motion is steady, the rates of effusion of two gases are still not simply proportional to the square roots of the densities, but are also dependent on the ratios of the two specific heats for the two gases. Considerable difficulty was experienced in obtaining apertures for which the viscosity effect was negligible, and a correction for viscosity is given, but is in most cases very small. The results show that, when compared with oxygen, the rate of effusion of argon is $3\frac{1}{2}$ per cent. faster than that calculated merely from the densities, and this is in qualitative accord with the theoretical deduction, or may be regarded as an additional proof of a high specific heat ratio. Hydrogen, oxygen, and carbon monoxide have rates of effusion in accord with those calculated, the specific heat ratios being also approximately equal for these gases; the effusion of carbon dioxide is, however, about 1 per cent. faster than that calculated from the density, and this is not ascribable to a high specific heat ratio. With helium, a relatively large viscosity correction has to be introduced, but the results are still not in accord with theory, the rate being slower than that calculated from the density. The author hence concludes that some factor has been omitted in the theoretical consideration, and that this is probably to be found in the Joule-Thomson effect. It is shown that a gas will effuse more slowly or more rapidly than an ideal gas, according as the Joule-Thomson effect is negative or positive. As for all the gases which Joule and Thomson examined, the constant was positive except for hydrogen, where the sign is uncertain, and as helium is even more "perfect" than hydrogen, it is probable that the sign is here negative, and that the anomalies of effusion are hence explicable. L. M. J.

Dissociation in Dilute Solutions at 0°. By W. C. DAMPIER WHETHAM (*Proc. Roy. Soc.*, 1900, 66, 192—203).—The degree of dissociation in dilute solutions, as determined by the conductivity at

18° or 25°, is not directly comparable with the value arrived at from freezing point experiments. The author has accordingly measured the conductivity at 0° of solutions of sulphuric acid, potassium chloride, barium chloride, copper sulphate, potassium permanganate, potassium ferricyanide, and potassium dichromate. The results are contained in a number of tables, and curves are drawn showing how α , the degree of dissociation, varies with the concentration. At 0°, α falls less rapidly with increasing concentration than at higher temperatures. The curve for sulphuric acid shows a maximum, in agreement with other observations at higher temperatures. The curve for potassium permanganate likewise shows a fall in the value of α for the most dilute solutions; this the author attributes to the action of the salt on the impurities left in the solvent.

It may be noted that the solvent and solutions were not allowed to come in contact with anything except platinum. J. C. P.

Relation of Taste of Acids to their Degree of Dissociation. II. By THEODORE W. RICHARDS (*J. Physical Chem.*, 1900, 4, 207—211).—Owing to the fact that the sour taste of acid salts is stronger than would be expected from the concentration of the hydrogen ions, Kahlenberg considered the explanation of the sour taste from the standpoint of the dissociation theory to be unsatisfactory (this vol., ii, 271). If, however, the sensation of taste is due to a chemical action between the substance and some constituent of the tongue surface, then the sensation may be accompanied by a removal of hydrogen ions, and hence further dissociation would occur in accord with the mass action law. It follows, therefore, that although the order of dissociation is correctly found, yet no quantitative connection can be obtained from the taste, and this is in accord with experiment. The above explanation is also in agreement with the paralytic effect of the sense of taste by concentrated solutions, and the author points out that hydrogen and hydroxyl ions, which are those possessing the most marked taste (Höber and Kiesow, *Abstr.*, 1899, ii, 206), are also those most capable of causing reactions in substances likely to be present in the tongue. Observed phenomena are hence not opposed to the dissociation theory (compare *Abstr.*, 1898, ii, 209).

L. M. J.

Simple Proof of van't Hoff's Osmotic Pressure Law. By KIKUNAYE IKEDA (*Zeit. physikal. Chem.*, 1900, 33, 280—286).—A siphon barometer tube, whose longer limb is of small bore, has its short wider limb closed by a moistened piece of bladder. The space in the wider limb unoccupied by mercury is filled with some gas, such as nitrogen, which is insoluble in water. When the whole is surrounded by a gas, for example, ammonia, which is soluble in water, the mercury rises in the longer limb owing to the diffusion of ammonia through the bladder, which thus acts as a semipermeable membrane. If A be the gas for which the membrane is permeable, and B the gas for which it is not permeable, it can be shown that the partial pressure (p) of B is independent of the concentration of A ; when this concentration is small, the relation $p = RTC$ holds, and from the above it must also hold when the concentration of A is great: in this way, the law can

be extended to the case of a solution, where A becomes the solvent and B the solute.

From the law $p = RTC$, Henry's law is deduced; the supposition that the absorption coefficient varies with the concentration of the gas is shown to be contrary to thermodynamical laws. J. C. P.

Hardness of Elementary Substances. By JOHANNES R. RYDBERG (*Zeit. physikal. Chem.*, 1900, 33, 353—359).—On the basis of Mohs' scale, and with the help of the existing data, an attempt is made to assign a numerical value for the hardness of the elements. The numbers obtained show that the hardness is a periodic function of the atomic weight. J. C. P.

Limited Chemical Reactions in Homogeneous Systems: Modulus Law. By A. PONSOT (*Compt. rend.*, 1900, 130, 829—832).

A theoretical paper in which the author deduces that in a system in equilibrium, the latter is independent of the pressure or of the presence of foreign substances, that if equilibrium is established at constant pressure, the volume is a minimum, and if at constant volume the pressure is a minimum. Thus the interaction of two salts in solution leads to a minimum volume, and hence at equilibrium $\Sigma dv/dm = 0$, where dv/dm is the coefficient of volume increase by addition of equivalents of the salts, and from this, as an immediate consequence, follows the additive effect of each radicle in causing change of volume in aqueous solution, and hence also change of density. That is, the coefficient of increase of density by the substitution of one radicle for another is independent of the radicle to which they are combined, and there is thus obtained what is termed the density modulus. Similarly, could be obtained modulus of vapour pressure, osmotic pressure, cryoscopic depression, &c. The author points out that these deductions are established without any presumption of dissociation. L. M. J.

Physical Reactions and the Mass Law. By AZARIAH T. LINCOLN (*J. Physical Chem.*, 1900, 4, 161—187).—Bancroft has shown that the relations between the compounds in certain cases of physical equilibrium may be represented by a modification of the usual mass-action formula, in which the exponential factors are not necessarily integers. Thus the relation between the concentrations x , y of two non-miscible liquids in a third consolute liquid of concentration z may be represented by the equation $x^\alpha y^\beta / z^{\alpha+\beta} = c$, and in this expression the concentrations may be expressed in units of any nature. If the liquids are mutually soluble, the equilibrium formula becomes $(x - s_2 y)^\alpha (y - s_1 x)^\beta / z^{\alpha+\beta} = c$, where s_1 and s_2 are the mutual solubilities (Bancroft, *Abstr.*, 1895, ii, 157). Experimental work has shown that these equations represent the facts with a fair degree of accuracy (Taylor, *Abstr.*, ii, 1898, 66, 213; Bathrick, *Abstr.*, 1897, ii, 135), and the author has examined the system water, benzene, alcohol, using pure compounds and employing great precautions to ensure accuracy in the equilibrium determinations. He finds the results to be in almost perfect accord with those given by the above expression, the differences being far smaller than in previous less accurate experiments and seldom reaching $\frac{1}{3}$ per cent., and he considers that if the

experimental difficulties could be more completely overcome, the accord would be still more perfect. Under these circumstances, he holds that the formula is not merely empirical, but represents the facts absolutely, and is hence the expression of an actual natural law.

L. M. J.

Equilibria in the System : Water, Phenol, and *d*-Tartaric or Racemic Acid. By FRANS A. H. SCHREINEMAKERS (*Zeit. physikal. Chem.*, 1900, 33, 74—77. Compare Abstr., 1899, ii, 739).—The influence of these two acids in raising the critical mixture temperature of water and phenol is equal, and much less than that of sodium chloride (*loc. cit.*). The critical mixture temperature of a water-phenol system containing 40.9 per cent. of tartaric acid (referred to water + tartaric acid) is about 30° higher than that of the water-phenol mixture alone. It appears that the elevation of the critical mixture temperature by a third substance is not only a function of the molecular weight of this substance, but depends also on other factors.

J. C. P.

Equilibria in the System : Water, Phenol, and Acetone. By FRANS A. H. SCHREINEMAKERS (*Zeit. physikal. Chem.*, 1900, 33, 78—98).—Mixtures of water and acetone of known composition were put in glass tubes, and known weights of phenol added; the tubes were closed and the temperatures observed at which the contents became homogeneous. A number of tables are thus obtained, and the corresponding curves drawn, showing how this temperature varies with the composition of the ternary mixture. The results are represented also by means of the triangular system, and the binodal curves are drawn for various temperatures: those for higher temperatures are enclosed by those for lower temperatures, and ultimately shrink to a point corresponding with the temperature 92°, and the composition 59 per cent. of water, 12 per cent. of acetone, and 29 per cent. of phenol. The chief feature of interest is that whilst above 68° separation into two layers takes place in none of the three binary systems water-acetone, water-phenol, and phenol-acetone, yet such a separation can take place up to 92° in mixtures containing all three substances.

The paper contains also a review of the author's experimental work on ternary systems (compare Abstr., 1897, ii, 483; 1898, ii, 329, 424, 564; 1899, ii, 739; this vol., ii, 135).

J. C. P.

The System : Water, Phenol, and Hydrochloric Acid. By W. H. KRUG and FRANK K. CAMERON (*J. Physical Chem.*, 1900, 4, 188—192).—If hydrochloric acid be added to the partially consolute mixture of phenol and water, the temperatures at which solid phenol can exist are altered. Since the system containing the solid phenol and two liquid phases is still monovariant, there is no definite melting point, but if the quantity of water is great compared with that of the phenol, the range of temperatures in which the solid phase persists becomes very small and a freezing point may be obtained. These values were determined for solutions containing from 0 to 130 grams of hydrochloric acid per litre, and a curve for temperatures against acid concentration is given; the temperature in water was found to

be $1\cdot365^{\circ}$, and in the most concentrated solution $17\cdot195^{\circ}$. The author suggests that from this curve the concentration of a hydrochloric acid solution may be quickly determined approximately from the freezing point of phenol in it.

L. M. J.

Velocity of Reaction of Acids in Organic Solvents. By M. GEIGER (*Gazzetta*, 1900, 30, i, 225—233).—The action of methyl alcoholic solutions of various acids on marble has been studied. For solutions of hydrogen chloride, the action is much slower than that of the aqueous acid; the initial velocity of reaction increases with the concentration of the solution, but less rapidly than the latter, so that the ratio of velocity to concentration shows a considerable diminution, owing to the decreasing dissociation of the acid in concentrated solutions. The reaction is greatly influenced by changes of pressure, an increase of 8 cm. of mercury above the atmospheric pressure serving to completely stop the action. Methyl alcoholic solution of hydrogen bromide attacks marble slightly more energetically than the chloride solution does, whilst with hydrogen iodide the reaction is a little slower. The initial velocities with which marble is attacked by these acids and by nitric acid, calculated for 1 c.c. of gas evolved per minute and per sq. cm. of surface, are given in the following table:

	4-Normal.	2-Normal.	Normal.	0·5-Normal.
HCl.....	0·26	0·20	0·16	0·12
HBr	0·31	0·22	0·17	—
HI	—	0·19	0·15	—
HNO ₃	—	0·25	0·14	—

From these values, it is seen that molecular solutions of these acids in methyl alcohol, when not too concentrated, give the same velocity of reaction with marble. Calcium sulphate being insoluble in methyl alcohol, the action of a methyl alcoholic solution of sulphuric acid on malachite was studied, and it was found that no action takes place; the same is the case if blocks of fused sodium carbonate are employed, although hydrogen chloride dissolved in methyl alcohol reacts readily with both these substances. Formic, acetic, and the chloroacetic acids are not dissociated in methyl alcohol solution and, as would hence be expected, do not attack marble or other carbonates. Zinc and magnesium are attacked much more readily than marble by a methyl alcoholic solution of hydrogen chloride.

T. H. P.

Hydrolysis in Organic Solvents. By A. CAJOLA and A. CAPPELLINI (*Gazzetta*, 1900, 30, i, 233—240. Compare Gennari, *Abstr.*, 1896, ii, 413).—The velocity with which methyl acetate is hydrolysed by caustic soda or potash, when dissolved in various alcohols, has been measured. The mean hydrolysis constants are given in the following table:

	Propyl alcohol.	<i>iso</i> Butyl alcohol.	<i>iso</i> Amyl alcohol
Soda.....	0·004371	0·00941	0·0117
Potash.....	0·004279	0·008285	0·01107

Thus the action is least energetic in propyl alcohol; this confirms the observations of Gennari (*loc. cit.*), who found that sodium hydroxide and

methoxide have a stronger hydrolysing action in ethyl alcohol than in methyl alcohol. In these alcohols, sodium hydroxide acts more energetically than potassium hydroxide. The hydrolysis of methyl acetate by means of methyl alcoholic solutions of sodium, potassium, barium, strontium, ammonium, and tetramethylammonium hydroxides has also been studied. Contrary to what would be expected on the dissociation hypothesis, sodium hydroxide has a hydrolysing effect less energetic than barium or strontium hydroxides. T. H. P.

Energy of Acids Dissolved in Mixtures of Organic Solvents and Water. By ANTONIO MORELLO (*Gazzetta*, 1900, 30, i, 257—264).—The inversion of cane sugar by means of hydrochloric and the chloroacetic acids has been measured in aqueous methyl alcohol (about 86 per cent.) and in aqueous acetone (about 70 per cent.) at the dilution $V=10$. The constants are as follows :

	86 per cent. methyl alcohol.	70 per cent. acetone.
HCl	0.00102	0.00122
$\text{CCl}_3 \cdot \text{CO}_2\text{H}$	0.000136	0.000121
$\text{CHCl}_2 \cdot \text{CO}_2\text{H}$	0.0000404	0.0000306
$\text{CH}_2\text{Cl} \cdot \text{CO}_2\text{H}$	—	0.00000416

The dissociation constants for hydrochloric and trichloroacetic acids, as deduced from the electrical conductivities, are for the aqueous methyl alcohol, 0.522 and 0.241, and for the aqueous acetone, 0.183 and 0.516 respectively. These results show that trichloroacetic acid, which in acetone is almost completely undissociated, in aqueous acetone suffers dissociation to a greater extent than does hydrochloric acid. Further, the values obtained from the electrical conductivities for hydrochloric and trichloroacetic acids differ both absolutely and relatively from those given by the inversion method. T. H. P.

Hydrolysis of Polysaccharides and Decomposition of Esters; Catalytic Action of some Metals. By OTTOKAR SULC (*Zeit. physikal. Chem.*, 1900, 33, 47—56).—Experiments, supplementary to those already described (Abstr., 1897, ii, 136), show that the inversion of sucrose is accelerated by silver, and specially by copper, both in the spongy form. Palladium is found to retard the hydrolysis by dilute acids of sucrose, maltose, and raffinose.

The decomposition of amyl acetate by water is very much slower in the presence of palladium, osmium, rhodium, iridium, copper, and silver; mercury is practically without effect. With isobutyl acetate, qualitatively similar results have been obtained. In view of the difficulty of securing uniform conditions, no attempt has been made to compare quantitatively the catalytic effect of the metals named. J. C. P.

Chemical Dynamics of the Condensation of Acetone. By KARL KOELICHEN (*Zeit. physikal. Chem.*, 1900, 33, 129—177).—In the presence of sodium hydroxide, acetone undergoes condensation with the formation of diacetonalcohol, and the author shows that this reaction is reversible, and that the final state is an equilibrium between the two products. In solutions, not too concentrated, it is shown that,

in accord with the mass action law, the equilibrium is expressed by the equation $(1-x)v/x^2=k$.

Although the velocity of the reaction is greatly influenced by the concentration of the catalyser, yet this has no effect on the final equilibrium, the velocity in either sense being equally affected. The velocity is approximately proportional to the concentration of the hydroxyl ions, and although for very weak bases the concordance is very imperfect, yet it is sufficient to indicate that the hydroxyl ion is the actual catalyser, and the discrepancies may be ascribed to the effect of the medium on the dissociation of the base, and to secondary reactions. The velocity of the reaction hence affords a means for the determination of the hydrolysis of sodium salts of weak acids, and the values so obtained for sodium carbonate are compared with those found by Shields (Abstr., 1893, ii, 418), with which, however, they are not in good accord, no explanation being given of the discrepancies. Normal salts have a marked action on the velocity, sodium chloride, nitrate, and thiosulphate causing a decrease, sodium sulphate an increase. The effect of temperature was also investigated; at low temperatures, the equilibrium is disturbed with increase of the alcohol. From the values of the equilibrium constants at 25.2° and 0° , the value $-77.4K$ is calculated for the heat of reaction. L. M. J.

Solubility of a Mixture of Salts having one Common Ion. By CHARLES TOUREN (*Compt. rend.*, 1900, 130, 908—911).—The solubility of a salt is diminished by the addition of another containing a similar ion, and in the case of slightly soluble salts, numerous experiments by Noyes with others have proved this diminution to be in accord with that predicted theoretically. The author extends the experimental work to very soluble salts, and has determined the solubility field for potassium nitrate and chloride, and nitrate and bromide. The experiments were made at temperatures of 14.5° and 25.2° , and in each case the results are shown by two curves, the first showing the decrease of solubility of nitrate by addition of the chloride or bromide, the second the decrease of solubility of the chloride or bromide by addition of nitrate; the intersection of these curves gives the composition of the solution in equilibrium with the two solid phases. It is seen that the first of these curves is identical for the two halogen salts, when the concentrations are expressed in molecular quantities, so that the molecules of chloride and bromide have equal effects in lowering the solubility of the nitrate, and are hence, even at high concentrations, equally dissociated. L. M. J.

Mechanism of Gelation in Reversible Colloidal Systems. By W. B. HARDY (*Proc. Roy. Soc.*, 1900, 66, 95—109).—The properties of the ternary system alcohol-gelatin-water have been studied. Below a certain temperature there are two phases, separated by a well-defined surface. The temperature of separation is raised by an increase in the proportion of alcohol or gelatin, and lowered by an increase in the proportion of water. Both phases are at first liquid, but with fall of temperature one becomes solid. The solid solution phase forms on the concave side of the surface of separation when the proportion of gelatin is small, on the convex side when the proportion

of gelatin is large. The more slowly the two phases are established, the less is the surface of separation, both in extent and curvature.

The system agar-water was also studied. A hydrogel of agar consists of a solid and a liquid part; each of these phases is a mixture of agar and water, but their composition depends on the ratio of agar to water in the whole mass, and more especially on the temperature. Taking the gaseous phase also into account, the hydrogel of agar is a system of three phases. The equilibrium is determined by the chemical potential of the components in the various phases, by two pressures and by temperature, other operating variables being capillary tension and the energy of the surface between the fluid and solid phases.

J. C. P.

Nature of so-called Colloidal Metallic Solutions. By RICHARD ZSIGMONDY (*Zeit. physikal. Chem.*, 1900, 33, 63—73).—A criticism of the conclusions of Stoeckl and Vanino (this vol., ii, 11). The author maintains that the gold solutions previously described by him (*Abstr.*, 1898, ii, 522) are really colloidal solutions, and not merely suspensions. The general characteristics of these two classes of liquids are discussed, and the tests applied by Stoeckl and Vanino are regarded as quite inadequate and inconclusive.

J. C. P.

Representation of the Periodic System of the Elements. By KARL SCHIRMEISEN (*Zeit. physikal. Chem.*, 1900, 33, 223—236).—The elements are represented in a system of circles, the angular displacement, in a clockwise direction, from the highest point of the circle, being proportional to the excess of the atomic weight above the initial value. The first circle embraces values from 3.96 (helium) to 20, so that lithium is situated at 68.8°, fluorine at 337.7°, &c.; the second circle is from 20 to 37.1; the third and fourth form a figure of eight, the upper circle embracing values between 37.1 and 48.3 and 72.7 and 83.9, the lower values between 48.3 and 72.7. A similar double set occurs for the fifth and sixth groups, 83.9 to 131.4, and for the eighth and ninth, 163 to 227, the tenth circle containing only two elements. The properties of elements may be deduced from their positions on these circles, and the author claims that his arrangement gives a better insight into the relations of the elements than any previously published, indicating more clearly the transition of properties of the elements of each group, and the properties of the different elements; that it locates the sub-groups more perfectly, connects coloured ions with the chemical properties, and indicates those places in the Mendeléeff system which it is probable will, or will not, be filled.

L. M. J.

Calibration of Glass Tubes, and some Compressibility Coefficients. By GEORGE A. HULETT (*Zeit. physikal. Chem.*, 1900, 33, 237—244).—The glass tube employed for compressibility determinations was calibrated by filling with mercury, and withdrawing equal quantities by means of a small capillary pipette, the tube being immersed horizontally in a specially constructed thermostat, and the position of the end of the mercury read by a microscope. The accuracy of the calibration was seen by the concordance of the corrected lengths

of a mercury thread in different parts of the tube. The apparent compressibility of mercury in this tube was found to be 0.78 cubic millimetres per c.c. per 100 atmospheres, and, accepting Amagat's value of 0.0₅39 for the absolute compressibility, this leads to the value of 0.39 cubic mm. per c.c. for the expansion of the glass tube per 100 atmospheres, which agrees well with the value 0.40, calculated from the dimensions of the tube. The compressibility of pure distilled water, containing dissolved air, was found to be 0.0₄453 at 9°, 0.0₄446 at 17°, and 0.0₄419 at 50°; and the compressibility of *p*-toluidine at 45° was found to be 0.0₄512.

L. M. J.

Inorganic Chemistry.

Vapour Density of Bromine at High Temperatures. By EDGAR P. PERMAN and G. A. S. ATKINSON (*Zeit. physikal. Chem.*, 1900, 33, 215—222).—A porcelain flask of about 1 litre capacity was heated in a muffle furnace, exhausted by a pump until the pressure was reduced to about one-sixth of an atmosphere, and then filled with bromine vapour, this process being repeated six times. The bromine vapour was then withdrawn by aid of the pump through absorption tubes, the flask filled with air, and the withdrawal repeated six times, the weight of the bromine being then found. Temperatures were determined by means of a thermo-electric junction calibrated by boiling selenium and melting potassium sulphate. The vapour densities so obtained were: 650°, 80.0; 830°, 79.7; 900°, 78.6; 950°, 77.5; 1015°, 76.7; 1050°, 74.3. At temperatures about 1040°, it was found that the density decreased from 76 at a pressure of 755 mm., to 71.8 at 47.3 mm., and curves are given showing these variations of density with temperature and pressure. The ratio of the velocities of dissociation and association are calculated for temperatures from 800° to 1050°, the ratio increasing over a hundred-fold within this range.

L. M. J.

Preparation of Hydrogen Sulphide and of its Solution. By CLEMENS WINKLER (*Ber.*, 1900, 33, 1040—1043).—The apparatus for the generation of hydrogen sulphide is the same as that previously described (*Zeit. anal. Chem.*, 1882, 21, 386). The gas is first passed through a leaden wash-cylinder, and then into a flat leaden vessel half filled with distilled water. When the water is saturated, a given volume may be withdrawn and replaced by pouring the same amount of distilled water through a funnel attached to the top of the vessel. The apparatus is thus kept filled with a saturated solution of hydrogen sulphide, which, for most qualitative purposes, is better than the gas.

J. J. S.

Combination of Metallic Iodides with Sulphur Dioxide. By E. PECHARD (*Compt. rend.*, 1900, 130, 1188—1189).—Sulphur dioxide is absorbed by an aqueous solution of potassium iodide, the

solution turning yellow, and finally orange, but this coloration is not due to free iodine. When sulphur dioxide is passed over solid potassium iodide at 0° , the salt turns yellow, and absorption of the gas readily takes place, with formation of the compound SO_2KI , which, on heating to 100° , readily parts with its sulphur dioxide. The following values (in cm. of mercury) were obtained for the vapour tension of this compound: 60 at 0° , 93 at 10° , 146 at 20° , 238 at 30° .

Similar compounds are formed with sodium, ammonium, barium, calcium, and silver iodides, the compound formed with the last being of a brick-red colour.

Hydriodic acid also readily absorbs sulphur dioxide, giving an orange-yellow solution from which free iodine is absent.

H. R. LE S.

Compounds of Telluric Acid with the Iodates. By RUDOLPH F. WEINLAND and H. PRAUSE (*Ber.*, 1900, 33, 1015—1018). The alkali iodates unite with telluric acid to produce compounds analogous to those formed with sulphuric, chromic, molybdic, and tungstic acids. *Potassium telluriodate*, $\text{K}_2\text{O}, \text{I}_2\text{O}_5, 2\text{TeO}_3, 6\text{H}_2\text{O}$, crystallises from a concentrated solution of its components in colourless prisms. The *rubidium* salt has a similar composition, whilst the *ammonium* salt has the formula $(\text{NH}_4)_2\text{O}, \text{I}_2\text{O}_5, 2\text{TeO}_3, 8\text{H}_2\text{O}$, and crystallises in irregular, six-sided plates. *Potassium telluridiiodate*, $\text{K}_2\text{O}, \text{I}_2\text{O}_5, \text{TeO}_3, 3\text{H}_2\text{O}$, crystallises from a solution of its components containing very slight excess of potassium hydroxide in vitreous, rhombohedral crystals. When recrystallised from water, a certain amount of the telluriodate is formed.

It has been found impossible to prepare sodium salts of similar composition. From analogy with the molybdoiodates, it seems probable that the two potassium salts have the constitutional formulæ $\text{KO} \cdot \text{IO}(\text{OH}) \cdot \text{O} \cdot \text{TeO}_2 \cdot \text{OH}$ and $\text{KO} \cdot \text{IO}(\text{OH}) \cdot \text{O} \cdot \text{TeO}_2 \cdot \text{O} \cdot \text{IO}(\text{OH}) \cdot \text{OK}$.

A. H.

Preparation and Properties of so-called Nitrogen Iodide. By FREDERICK D. CHATTAWAY and KENNEDY J. P. ORTON (*Amer. Chem. J.*, 1900, 23, 363—368. See *Proc.*, 1899, 15, 17).

Action of Reducing Agents on Nitrogen Iodide. By FREDERICK D. CHATTAWAY and HENRY P. STEVENS (*Amer. Chem. J.*, 1900, 23, 369—376. See *Proc.*, 1899, 15, 17).

Preparation of Phosphorus Trisulphide. By EDM. SPRINGER (*Chem. Centr.*, 1900, i, 712; from *Pharm. Zeit.*, 45, 164).—The loss due to the burning of the mixture of red phosphorus and sulphur in the preparation of phosphorus trisulphide is avoided by at first only heating a small portion of the mixture in a Hessian crucible until combination takes place, removing the burner and then adding the rest of the mixture in small portions at a time. If the first charge takes fire, it is extinguished by means of sand, and after each subsequent addition the lid is replaced on the crucible. The action takes place quietly, causing only a slight puff and formation of fume.

E. W. W.

Electrolysis of Solutions of Alkali Chlorides. By HEINRICH WOHLWILL (*Zeit. Elektrochem.*, 1899, 6, 227). By FRITZ FOERSTER (*ibid.*, 253).—A criticism of Foerster's results relating to the electrolytic formation of chlorates (*Abstr.*, 1899, 88, 278; this vol., ii, 72) and a reply thereto. T. E.

Decomposition of Sodium Thiosulphate by Acids. By HELMUTH VON OETTINGEN (*Zeit. physikal. Chem.*, 1900, 33, 1—38).—According to the ionic theory, the decomposition is represented by the equation $\overline{\text{S}_2\text{O}_3} + \overline{\text{H}}^+ = \overline{\text{HSO}_3} + \text{S}$, so that the concentration (x) of the hydrogen ions should have an influence on the progress of the reaction. If y be the time that elapses between the acidification of a dilute sodium thiosulphate solution and the appearance of turbidity, experiments show that for hydrochloric acid $y = 1/[A \log. (1 + bx)]$, where A and b are constants. When, instead of hydrochloric acid, solutions of oxalic, dichloroacetic, or trichloroacetic acid, with an equal concentration of hydrogen ions, are employed, the value of y remains unchanged. This result is regarded as a confirmation of the electrolytic dissociation theory. The initial presence of sodium sulphite hinders the appearance of turbidity, but in this case also the above logarithmic equation is found to be satisfied, provided allowance be made for the appropriation of $\overline{\text{H}}^+$ ions by the $\overline{\text{SO}_3}$ ions, to form either $\overline{\text{HSO}_3}$ ions or undissociated molecules of sulphurous acid. The point of equilibrium of the reversible reaction—thiosulphate=sulphite + sulphur—cannot be determined, owing to the interaction of thiosulphate and sulphite (*Colefax, Trans.*, 1892, 61, 176).

Conductivity experiments show that not only in the appearance of turbidity, but also in the further progress of the reaction, the concentration of the hydrogen ions is the determining factor; isohydric acid solutions have an equal effect on the velocity of decomposition.

J. C. P.

Solubility of Sodium Tungstate in Water and the Density and Refractive Indices of its Solutions. By BRONISLAW PAWLEWSKI (*Ber.*, 1900, 33, 1223—1224).—A table is given of densities and refractive indices at 20° of solutions containing from 2.21—38.43 per cent. of sodium tungstate, Na_2WO_4 (corresponding with a range of 2.48—43.14 per cent. of $\text{Na}_2\text{WO}_4 + 2\text{H}_2\text{O}$). W. A. D.

Change of Volume accompanying Fusion of Rubidium. By MORITZ ECKARDT (*Ann. Phys.*, 1900, [iv], 1, 790—792).—By means of a dilatometer, the increase of volume on fusion was found to be 0.01657 c.c. for 1 gram of rubidium. The melting point was 37.8°, and 5 to 6 grams were used in the experiments. The corresponding increase of volume for caesium is 0.01393 c.c. for 1 gram of the metal.

J. C. P.

Electrolysis of the Bromides of the Alkaline Earth Metals. By JON SARGHEL (*Zeit. Elektrochem.*, 1899, 6, 149 and 173).—Solutions of the bromides of calcium, magnesium, and barium (10 and 20 per cent.) are electrolysed in a cell with platinum electrodes, and without

a diaphragm. The influence of temperature, current density, and the addition of alkalis to the solutions is investigated.

Calcium Bromide.—In neutral solutions, bromate and small quantities of hypobromite are formed. The highest current efficiency (90·8 per cent. of the theoretical amount) was obtained with a 10 per cent. solution at 75°; the electrodes were of equal size, and the current density 0·07 ampère per sq. cm. About 3 per cent. of the active bromine was present as hypobromite, the remainder as bromate. At higher temperatures, the yield is considerably smaller; at lower temperatures, it is slightly smaller. Increased concentration and increased current density both diminish the current efficiency. When lime is added to the solution, the efficiency also falls, owing to the increased formation of hypobromite and its subsequent reduction at the cathode. If a cathode with a smooth surface is used (instead of one with a rough surface), the calcium hydroxide, instead of adhering to the metal, passes into the solution, giving rise to the formation of hypobromite, and a consequent diminution of efficiency.

Magnesium Bromide.—More hypobromite and less bromate are formed when solutions of magnesium bromide are electrolysed than is the case with CaBr_2 . The total current efficiency is also less since, owing to the smaller solubility of magnesia, a considerable quantity of bromine escapes conversion into hypobromite. The best result (89·1 per cent. of the theoretical amount) was obtained with a 10 per cent. solution, current density at the cathode 0·07 ampère per sq. cm., at the anode 0·007 ampère per sq. cm., temperature 50°, E.M.F. 5·5 to 12·5 volts. In this experiment, 10·7 per cent. of the active bromine was present as hypobromite; the remainder as bromate. The influence of temperature is the same as in the case of calcium bromide. The efficiency is improved by an increase of the current density or by adding small quantities of magnesia to the solution.

Barium Bromide.—Owing to the ready solubility of barium hydroxide, considerable quantities of hypobromite are formed, and owing to the ease with which this substance is again reduced at the cathode, the total current efficiency is low. T. E.

Hydrated Calcium Peroxides. By ROBERT DE FORCRAND (*Compt. rend.*, 1900, 130, 1308—1311. Compare this vol., ii, 129, 277, 344).—Hydrated calcium peroxides are precipitated on adding hydrogen peroxide to saturated solutions of calcium hydroxide, just as in the preparation of the corresponding strontium and barium compounds.

When hydrogen peroxide ($\frac{1}{2}$ mol.) reacts with calcium hydroxide (1 mol.) in dilute solutions, the heat developed is 6·877 Cal.; the product is a fine, light powder which, when dried on porous plates, gives numbers corresponding with $\text{CaO}_{1\cdot842}\cdot 2\cdot 31\text{H}_2\text{O}$; it differs from the strontium and barium compounds both in composition and in heat of formation. A similar result is obtained when 1 or 2 mols. of hydrogen peroxide are employed. When 3 or 4 mols. of this reagent are added at 13—14°, the compound $\text{CaO}_{2\cdot06}\cdot 8\cdot 57\text{H}_2\text{O}$ is obtained, the heat of formation being 24·666 Cal.; this product is therefore an analogue of the hydrated strontium and barium peroxides, which have a similar

heat of formation and contain approximately the same amount of water; at 20°, the reaction takes a slightly different course, the substance produced being more pulverulent, and having the following composition, $\text{CaO}_{1.91}, 2\text{H}_2\text{O}$. G. T. M.

Radio-active Barium. By BÉLA VON LENGYEL (*Ber.*, 1900, 33, 1237—1240).—Uranium nitrate was fused with 2—3 per cent. of barium nitrate, subsequently converted by heat into the oxide, and the latter fused in an electric arc; the mass was then dissolved in nitric acid, most of the barium nitrate allowed to separate, and the decanted clear solution precipitated with sulphuric acid. The barium sulphate so obtained was strongly radio-active, and this was also the case with the barium carbonate and chloride obtained therefrom. In the author's opinion, this "synthesis" of radio-active substances, although merely preliminary, renders the existence of radium and polonium doubtful (compare P. and S. Curie, this vol., ii, 81—83, 126, 254). W. A. D.

Action of Chlorine on Cupric Hydroxide suspended in Potassium Hydroxide. By F. MAWROW (*Zeit. anorg. Chem.*, 1900, 23, 233—235).—Hydrated cupric oxide, $6\text{CuO}, \text{H}_2\text{O}$, is obtained by the action of chlorine on cupric hydroxide suspended in potassium hydroxide. The product is a dark brown powder, and a complete conversion of the cupric hydroxide is only obtained by employing a large amount of potassium hydroxide, an excess of chlorine, and heating the mixture at 50—60°. No indication was observed of the formation of the red solution described by Krüger (*Zeit. anorg. Chem.*, 2, 658), which is supposed to contain a salt of cupric acid.

E. C. R.

Lead Selenides and Chloroselenides. By HENRI FONZES-DIACON (*Compt. rend.*, 1900, 130, 1131—1133).—Crystalline lead selenide, PbSe , was first obtained by Margottet, who prepared it by heating the amorphous compound in a current of hydrogen. It may also be produced by the following methods: (1) reduction of lead selenate by hydrogen at a bright red heat; (2) reduction of the selenate by carbon in the electric furnace; (3) action of hydrogen selenide on the vapour of lead chloride. The compound crystallises in cubes or in needles composed of rectangular lamellæ, is easily friable, and has a sp. gr. 8.10 at 15°. The selenide is decomposed by heated hydrogen chloride, oxygen, chlorine, steam, and the vapour of phosphorus trichloride. It is readily attacked by nitric and sulphuric acids, but only slowly decomposed by concentrated hydrochloric acid.

Lead chloroselenide, produced by the action of hydrogen selenide on a solution of lead acetate containing hydrochloric acid, is obtained as a red precipitate; it may also be prepared by passing the vapour of phosphorus trichloride over gently warmed amorphous lead selenide. This substance is converted into the selenide by the action of heat, boiling water, hydrogen selenide, sodium thiosulphate, and concentrated solutions of potassium hydroxide. G. T. M.

Formation and Transformation of the Double Salts of Thallium and Silver Nitrates. By C. VAN EIJK (*Proc. K. Akad. Wetensch. Amsterdam*, 1900, 2, 480—484).—Fused mixtures of thallium and silver nitrates were examined in order to ascertain whether a double salt separates out on cooling. Although such a substance was not isolated, yet the melting point determinations showed that, when fused mixtures containing 47—53 per cent. of silver nitrate were cooled down to 80—85°, a double salt separates out, the separation being most rapid at 82·8°. The discontinuity in the melting point curve corresponding with the formation of the double salt, is represented by a horizontal line connecting the portion of the curve representing the separation of solid thallium nitrate from that indicating the crystallisation of the silver salt.

Silver and thallium nitrates are rhombic at the ordinary temperature, but, at 159° and 142° respectively, undergo a structural change and become rhombohedral; if the crystals of either contain any impurity, the transition temperature is either raised or depressed, and this phenomenon is utilised in testing the purity of the solid separating from the fused mixtures of the two salts. Crystals taken from mixtures containing excess of silver nitrate undergo transformation at 160°, and appear to contain 80—100 per cent. of the silver salt; the solid separating from mixtures containing excess of thallium nitrate is transformed at 142°, and is therefore pure thallium salt.

It follows from this that mixed crystals are scarcely formed at all, and that the solidified mixtures are conglomerates of the double salt with excess of silver nitrate or thallium nitrate. At 26—27°, the double salt undergoes a transformation, the precise nature of which is not understood; this change proceeds very slowly, and is detected by dilatometric experiments; the volume of the admixed substance greatly diminishes, whilst that of the admixed silver or thallium salt remains unaltered.

G. T. M.

The Cerite Earths. By OTTO N. WITT and WALTER THEEL (*Ber.*, 1900, 33, 1315—1324).—Cerium can readily be separated from the other metals which usually accompany it in the cerite earths by means of ammonium persulphate. When a solution of a normal cerous salt is boiled with ammonium persulphate, oxidation occurs and a ceric salt is formed, which is at once decomposed by the water present into a basic ceric sulphate and free acid. If this acid is neutralised as fast as it is produced, the reaction becomes quantitative, and the whole of the cerium present is precipitated as basic ceric sulphate, whilst the other earths remain in solution. The normal salts of the cerite earths have a faintly acid reaction to litmus paper, but do not react with Congo paper, and the boiling liquid must therefore be maintained faintly acid to litmus, but neutral to Congo paper by the cautious addition of sodium carbonate solution or finely powdered calcium carbonate until the reaction is complete. The precipitate can readily be washed and the filtrate is quite free from cerium. The method is of special value for use in conjunction with Scheele's method of fractionation of the cerite earths, according to which the cerium is retained in the mixture of nitrates, whilst the lanthanum is gradually

removed, the result being solutions of neodymium and praseodymium mixed with cerium, from which the latter can then be removed by the persulphate process.

A. H.

Microchemical Researches on Yttrium, Erbium, and Didymium. By M. E. Pozzi-Escot and H. C. Couquet (*Compt. rend.*, 1900, 130, 1136).—When treated with ammonium chromate, yttrium salts yield a chromate separating in elongated, hexagonal crystals having a violet tint; the corresponding didymium salt is obtained in orange, prismatic crystals exhibiting twinning, whilst the erbium compound crystallises with great difficulty and is usually amorphous.

With a solution of chromium trioxide in concentrated sulphuric acid, filiform crystals are obtained from yttrium salts, large, ill-defined crystals from erbium compounds, and amorphous precipitates gradually becoming crystalline from didymium derivatives.

These rare earth metals also form characteristic double chlorides with palladium chloride.

G. T. M.

Samarium. By EUGÈNE DEMARÇAY (*Compt. rend.*, 1900, 130, 1185—1188. Compare this vol., ii, 347).—The intermediate fractions obtained in the separation of neodymium and samarium show no indication of the presence of a third element.

A nitric acid solution of the samarium salts shows the following bands: λ 559 (feeble), 529 (very feeble, narrow), 498 (feeble, rather narrow), 476 (strong, diffused), 463 (very strong, rather wide), 453 (very feeble, narrow), 443 (very wide and diffused), 417 (very strong, wide), 407 (feeble, narrow and joining the next), 402 (very strong, wide), 390 (feeble, very wide and diffused), 375 (strong, wide), 362 (strong, wide).

The reversion spectra of the salts either in hydrochloric or nitric acid solution gave the three following bands: λ 644 (wide), 600 (middle of the principal band which extends from 610 to 593), and 564 (middle of the third band). No fourth band corresponding with the 614.4 band of Lecoq de Boisbaudran could be detected in the pure samarium examined.

Analyses of samarium sulphate gave numbers varying between 148 and 147.2 ($O=16$) for the atomic weight of the metal; the author is, however, not satisfied with the method employed.

The *double nitrate*, $\text{Sm}(\text{NO}_3)_3 \cdot 3\text{Mg}(\text{NO}_3)_2 \cdot 24\text{H}_2\text{O}$, forms large, pale yellow, rhombohedral crystals melting at $94.5\text{--}93.5^\circ$. The *nitrate*, $\text{Sm}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$, forms thick, orange-yellow crystals which are very hygroscopic and melt at $78\text{--}79^\circ$.

H. R. LE S.

Nature of the Process which occurs at the Aluminium Anode. By KONRAD NORDEN (*Zeit. Elektrochem.*, 1899, 6, 159 and 188).—When aluminium is used as anode in the electrolysis of dilute sulphuric acid, it becomes coated with a substance possessing a high resistance which gives rise to an apparent polarisation of some 20 to 30 volts. The author shows that when an aluminium wire is used alternately as anode and as cathode, the skin formed when the wire is anode is detached from the metal when it is used as cathode, and that when it is again used as anode a fresh coating forms under the old one.

By many repetitions of the process, the skins peel off and a quantity sufficient for an analysis may be collected. Analyses of the coatings formed with different current densities and different concentrations of acid agree well with each other, the average result being: Al_2O_3 , 69.8 per cent.; SO_3 , 13.2 per cent.; H_2O , 14.8 per cent.; SiO_2 , 2.2 per cent. The silica is doubtless due to oxidation of the silicon contained in the aluminium used. In the remaining substance, some of the aluminium is present in the form of small particles of metal. A mixture of a compound, $\text{Al}_2\text{O}(\text{SO}_4)_2 \cdot \text{H}_2\text{O} + 5\text{Al}_2(\text{OH})_6$, with 9.25 per cent. of metallic aluminium would have the composition indicated by the analyses. T. E.

Preparation of Aluminium [Sulphide, Selenide, Phosphide, and Arsenide]. By HENRI FONZES-DIACON (*Compt. rend.*, 1900, 130, 1314—1316).—Aluminium sulphide, Al_2S_3 , is readily prepared when a mixture containing equivalent proportions of precipitated sulphur and fine aluminium powder is ignited by means of burning magnesium; the combustion is propagated throughout the mass, and a compact, yellowish-grey product is obtained, which is decomposed by water, yielding hydrogen sulphide. A mixture of antimony sulphide and aluminium, when treated in this way, yields aluminium sulphide and metallic antimony.

Aluminium selenide, Al_2Se_3 , is obtained in a precisely similar manner as a yellowish-grey, fibrous mass, which evolves hydrogen selenide when treated with water.

Aluminium phosphide, Al_2P_3 , is prepared by igniting an intimate mixture of aluminium and red phosphorus; when moistened, it evolves non-inflammable hydrogen phosphide, the yield of this gas being practically theoretical.

Aluminium arsenide is a black, friable mass, produced from a mixture of aluminium and metallic arsenic; the hydrogen arsenide liberated from this compound by the action of water is almost wholly absorbed by copper sulphate, and the decomposition is quantitative.

A mixture of antimony and aluminium is not ignited by a fuse of magnesium or an aluminium cartridge (a mixture of aluminium and barium dioxide fastened to a strip of magnesium); its combustion may, however, be effected by adding a small quantity of sodium peroxide; the product is a black, friable mass, which, when treated with water, evolves a considerable amount of hydrogen antimonide. G. T. M.

Manganous Fluoride. By HENRI MOISSAN and VENTURI (*Compt. rend.*, 1900, 130, 1158—1162).—*Manganous fluoride*, MnF_2 , is best prepared by dissolving manganese in dilute hydrofluoric acid contained in a silver basin, which is kept cool by a rapid current of cold water; on boiling the resulting solution, the manganous fluoride is precipitated as a white, crystalline powder, which is collected and dried at 120° .

Manganese is readily attacked by hydrogen fluoride with the development of much heat, and manganous fluoride is thus obtained as a rose-coloured, fused mass. Pure manganous fluoride may also be formed by heating hydrated manganese silicofluoride to 1000° in a current of hydrogen fluoride. When manganous carbonate is dissolved

in dilute hydrofluoric acid, the resulting solution contains the hydrated fluoride; when the solution is boiled, a certain amount of the anhydrous salt is deposited.

Manganous fluoride may be recrystallised from fused manganous chloride, when it is obtained as rose-coloured prisms of sp. gr. 3.98, and melting at 856°. Manganous fluoride is completely reduced by hydrogen at 1000°, but only very slowly at 500°; it is only slowly decomposed by fluorine in the cold, but readily on heating, manganese trifluoride being formed (this vol., ii, 280).

It is not attacked by chlorine in the cold; but at 1200° partial decomposition occurs, manganous chloride being formed. Dry oxygen acts only slowly on manganous fluoride at 400°, but at 1000° it is completely decomposed, and manganese tetroxide is formed; when heated to 1000° in an atmosphere of sulphur, it is rapidly converted into green manganous sulphide. It is not decomposed by carbon at 1200°, but at 1000° both silicon and boron readily decompose it, with formation, in the first case, of manganese silicide, and in the second, of boron fluoride and manganese boride. When manganous fluoride is boiled with water, manganese oxyfluoride and hydrofluoric acid are first produced; if the boiling is continued, then a mixture of hydrated manganese fluoride and oxyfluoride is deposited. At 1200–1300°, manganous fluoride is converted by steam into manganous oxide, and by hydrogen sulphide into green manganous sulphide. It is sparingly soluble in liquid ammonia, a crystalline *powder* being produced, probably of the composition $3\text{MnF}_2 \cdot 2\text{NH}_3$, which slowly evolves ammonia. When heated at 1200° in an atmosphere of ammonia, the fluoride is partially reduced.

Sodium, potassium, aluminium, and magnesium reduce manganous fluoride below a red heat, cold concentrated nitric acid and hydrochloric acid dissolve it readily, and dilute hydrochloric acid and acetic acid only slowly; but hydrofluoric acid is without action on it, and sulphuric acid decomposes it with evolution of hydrogen fluoride. It is decomposed by fused alkali carbonates, potassium hydroxide, potassium nitrate, and potassium chlorate, and with chlorine or bromine water manganese dioxide and hydrofluoric acid are produced. Manganous fluoride is practically insoluble in water, alcohol, or ether.

H. R. LE S.

Cause of the Evolution of Oxygen when Oxidisable Gases are Absorbed by Permanganic Acid. By HARMON N. MORSE and H. G. BYERS (*Amer. Chem. J.*, 1900, 23, 313–322. Compare Morse and Reese, *Abstr.*, 1898, ii, 588).—It is shown that no oxygen is liberated, either during the absorption of carbon monoxide by neutral aqueous potassium permanganate, or during subsequent prolonged agitation of the neutral solution with the manganese dioxide thus precipitated; if, however, the solution is acidified with sulphuric acid immediately after the absorption, there is a liberation of oxygen just as when the gas is absorbed by an acid solution. The amount of oxygen liberated within a given period increases with the concentration of the solution, and the rate of evolution in any given case diminishes with time, the decrease being most marked in the more

concentrated solutions. With a fixed quantity of carbon monoxide, the quantity of oxygen liberated during absorption with initially acid solutions of potassium permanganate increases with the concentration of the solutions; the same is true of the amount liberated in a given period after the absorption is complete, and the rate of evolution diminishes with time just as in the foregoing case of solutions initially neutral and subsequently acidified. The authors therefore conclude that in acid solution the liberation of oxygen is due to the reduction of the permanganic acid by the precipitated manganese dioxide, rendered active by the sulphuric acid present; the fact that no oxygen is liberated in neutral solutions may be due to either potassium permanganate being more stable than permanganic acid, or to the precipitated manganese dioxide being "saturated" with alkali, or to both causes combined. The falling off with time of the reducing power of the manganese dioxide in acid solution is explained by assuming the initial activity of the manganese dioxide molecules to be due to their simplicity; as the molecules become more complex owing to polymerisation, so do they lose their power of reduction. It is noteworthy that whilst the oxide formed in acidified solutions is, in general (especially in the more concentrated solutions), more active during the first 24 hours than that formed in neutral solutions, the converse is true after 150 hours.

W. A. D.

Revision of the Atomic Weight of Iron. By THEODORE W. RICHARDS and GREGORY P. BAXTER (*Zeit. anorg. Chem.*, 1900, **23**, 245—254).—The method employed is the reduction of ferric oxide to iron in a current of hydrogen. The operation is carried out in a porcelain tube at 900°, and a considerable time is required to effect complete reduction. In the first series of experiments, the iron, purified by electrolytic deposition, was dissolved in nitric acid, the solution precipitated with ammonia, and the precipitate of hydroxide washed with water and converted into oxide by heating at 900° to a constant weight. Two experiments with this oxide gave the mean value $\text{Fe} = 55.900$ ($\text{O} = 16$). In the second series, the ferric oxide was prepared by heating the carefully purified nitrate at 900° to a constant weight. The mean of five experiments gave the value $\text{Fe} = 55.883$.

The ferric oxide prepared from the nitrate was more easily reduced than that prepared from the hydroxide. A careful examination of the ferric oxide showed that it contained only a very minute quantity of included gases, chiefly nitrogen, and also a very minute quantity of platinum, derived from the vessel employed, the total impurities being such as to increase the results by only 0.01 per cent.

E. C. R.

Thermochemistry of Iron and Steel. By EDWARD D. CAMPBELL (*J. Amer. Chem. Soc.*, 1900, **22**, 205—206).—The author now finds that the heat of solution of steel in slightly acid ammonium copper chloride solution does not depend to any considerable extent on the heat or mechanical treatment to which the metal has been subjected, or on its chemical composition, the extreme variation being less than

2 per cent. He therefore withdraws his previous paper on this subject (Campbell and Thompson, Abstr., 1898, ii, 323). E. G.

Allotropic Transformations of Iron and Nickel Alloys. By L. DUMAS (*Compt. rend.*, 1900, 130, 1311—1314. Compare Abstr., 1899, ii, 352, 630).—The paper contains the diagrams and tabulated results of experiments on the transformation points of alloys of iron and nickel containing traces of carbon and manganese, and in one case chromium. The diagrams indicate that the curves of the transformation points of iron (non-reversible transformation) are distinct from those of nickel (reversible transformation), and there is therefore no minimum transformation temperature corresponding with the existence of a eutectic alloy. Nickel lowers the transformation points of iron, and iron lowers those of nickel, although at first it raises them. The magnetism of alloys, containing less than 25 per cent. of nickel, which have not been cooled below 0° , is entirely due to the iron present; when the percentage is greater than 26, the magnetic properties are wholly derived from the nickel; the alloys containing intermediate amounts of nickel are almost non-magnetic at ordinary temperatures, owing to the simultaneous depression of the transformation points of both their constituents. G. T. M.

Electro-deposition of Chromium. By SHERARD COWPER-COLES (*Chem. News*, 1900, 81, 16—18).—Electro-deposited chromium is comparatively soft, and tarnishes; a bright deposit can be obtained from a solution of 25 parts of chromium chloride in 75 parts of water, working at 190° F. with a current of 40 to 50 ampères per square foot. In the cold, gas is evolved at both electrodes, but no metallic deposit is obtained until excess of hydrochloric acid is added. A solution of 100 parts of chrome alum in 100 parts of water with 12 parts of barium sulphate does not yield a metallic deposit by electrolysis.

D. A. L.

Enantiotropy of Tin. IV. By ERNST COHEN (*Proc. K. Akad. Wetensch. Amsterdam*, 1900, 2, 464—467. Compare this vol., ii, 83 and 212).—Another case of 'tin plague' infection is noticed, and emphasis is laid on the fact that the corrosion of tin is independent of the mode of preparation of the metal. The occurrence of 'tin plague' in organ pipes suggested that the conversion of the white into the grey modification below 20° might be accelerated by mechanical vibration, but a test experiment gave a negative result. J. C. P.

Hydrolysis of some Chlorine Compounds of Platinum, Gold, and Tin on Standing, and under the Influence of Light. By FRIEDRICH KOHLRAUSCH (*Zeit. physikal. Chem.*, 1900, 33, 257—279).—Platinic chloride crystallises with $5\text{H}_2\text{O}$, but the fifth molecule cannot be removed without decomposition of the chloride. Hittorf and Salkowski (Abstr., 1899, ii, 398), and Dittenberger and Dietz (Abstr., 1899, ii, 629), have shown that in the electrolysis of this compound the platinum goes to the anode. These facts point to the existence of an oxy-acid, PtCl_4OH_2 . The author finds that even in the dark the conductivity of solutions of this compound increases, especially when they are left in contact with the electrodes; the conductivity rises

rapidly when the solutions are exposed to sunlight; red, yellow, blue and white light are increasingly efficient in producing the hydrolysis that this increase of conductivity points to. When the limit of hydrolysis in dilute solutions is reached, it seems as if all the chlorine were present as hydrogen chloride; in more concentrated solutions, the hydrolysis does not go so far. The numbers obtained for the molecular conductivity of freshly prepared solutions agree fairly well with the supposition that PtCl_4OH_2 is a moderately dissociated monobasic acid. The hydrolysis is accompanied by a change in colour from an almost greenish-yellow to a bright orange, and in the more dilute solutions a sort of fluorescence is observed, which the author attributes to the separation of finely divided particles, possibly of platinic hydroxide. Similar changes of conductivity take place in solutions of chloro-platinic acid of less than 1/10th normal strength; stronger solutions are stable and not affected by light. For a freshly-prepared solution containing 0.0002 gram-equivalents per litre, $\mu = 380$; when hydrolysed by light, μ for the same solution = 1048; here again, it seems as if all chlorine were present as hydrogen chloride.

In solutions of gold chloride, light causes no hydrolysis; a slight increase in conductivity with time is set down to the action of the electrodes.

The change in conductivity of stannic chloride solutions with time has been accurately traced; the change becomes less rapid as hydrolysis proceeds, and light is found to have no hydrolysing influence. At higher temperatures, the rate of hydrolysis is much increased. Comparison of the results for platinic and stannic chlorides show that the two compounds are essentially different in type.

The temperature coefficient of the conductivity has been determined for the above solutions, and found to agree approximately with the value obtained in the case of acids generally. J. C. P.

[Similar experiments on the hydrolysis of stannic chloride solutions have been made by Kowalewsky (this vol., ii, 256).—ABTRACTOR.]

Mineralogical Chemistry.

Magnetic Iron-Ores from Eastern Ontario. By FREDERICK J. POPE (*Trans. Amer. Inst. Mining Eng.*, California Meeting, Oct. 1899, 34 pp.).—These ores occur in gneisses and schists, or at the contacts of these with crystalline limestone, and also in gabbros and anorthosites. Descriptions and twelve detailed analyses are given of the ores from several mines. The magnetites occurring in the gabbro differ from the others in being titaniferous and in containing small amounts of vanadium (up to 0.63 per cent. V_2O_5) and of nickel and cobalt (compare Abstr., 1899, ii, 109; this vol., ii, 283).

Details are given of the methods used in estimating titanium and vanadium, and also for the preparation of pure vanadic oxide from these ores.

L. J. S

Minerals from Narsarsuk, S. Greenland. By GUSTAV FLINK (*Meddelelser om Grønland*, 1899, [1900], 24, 7—180).—A detailed description is given of 34 mineral species, of which 9 are new, collected by the author in 1897 on the plateau of Narsarsuk, near Julianehaab, S. Greenland. The minerals occur in drusy cavities bounded by large crystals of microcline and ægirite, which locally form pegmatite masses in the syenite of the region; this on weathering leaves the minerals in the coarse gravel on the surface. Analyses, several of which were made by R. Mauzelius, are given of the following minerals.

Rhodochrosite occurs as small rhombohedra, and is frequently altered to a black, powdery substance. Analyses of the least altered material gave:

MnO.	FeO.	CaO.	O, CO ₂ , H ₂ O.	Total.	Sp. gr.
57·06	15·76	2·68	[24·50]	100·00	3·666

Parisite (compare Abstr., 1895, ii, 401).—The parisite from Greenland differs from the original parisite from Colombia in several of its most important characters. The former has a rhombohedral instead of hexagonal development, and although several crystal forms are present few are common to both occurrences; it is also frequently twinned on (111) and has no cleavage, but there is sometimes a parting parallel to (111). The sp. gr. (3·902 Greenland, 4·3915 Colombia) and refractive indices also differ. Formula, $\text{CeFCa}(\text{CO}_3)_2$. The Colombian mineral has the formula $(\text{CeF})_2\text{Ca}(\text{CO}_3)_3$ (Abstr., 1899, ii, 600), but there is, however, not sufficient reason to consider that these are two distinct minerals. Analysis:

CO ₂ .	Ce ₂ O ₃ .	(La, Di) ₂ O ₃ .	Y ₂ O ₃ .	CaO.	Na ₂ O.	K ₂ O.	F.	Total, less O for F.
26·54	28·14	22·88	1·23	17·13	0·19	0·12	5·82	99·60

Cordylite (barium-parisite).—This new mineral occurs as small, hexagonal, club-shaped crystals, with [$a:c=1:3·3865$; for parisite, $a:c=1:3·3645$]. The crystals are pale wax-yellow, clear and transparent, and there is a distinct basal cleavage. Optically uniaxial and negative. Sp. gr., 4·31. Formula, $(\text{CeF})_2\text{Ba}(\text{CO}_3)_3$, which is the same as that of the Colombian parisite with barium in place of calcium. Analysis:

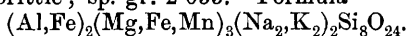
CO ₂ .	ThO ₂ .	Ce ₂ O ₃ .	(La, Di, &c.) ₂ O ₃ .	Y ₂ O ₃ .	FeO.	BaO.	CaO.	H ₂ O.	F.	Insol.
23·47	0·30	23·72	25·67	trace	1·43	17·30	1·91	0·80	[4·87]	2·58

Ancylite.—The orthorhombic crystals of this new mineral are octahedral in habit, with markedly curved faces of the forms {101} and {011}; [$a:b:c=0·916:1:0·9174$]. The colour is light yellow inclining to orange, but also brownish or greyish. Sp. gr. 3·95. Formula, $4\text{Ce}(\text{OH})\text{CO}_3, 3\text{SrCO}_3, 3\text{H}_2\text{O}$. Traces of Y_2O_3 , MnO and fluorine are also present. The mineral is somewhat allied to the Norwegian *weibeyite*. Analysis:

CO ₂ .	ThO ₂ .	Ce ₂ O ₃ .	(La, Di, &c.) ₂ O ₃ .	FeO.	SrO.	CaO.	H ₂ O.	Insol.	Total.
23·28	0·20	22·22	24·04	0·35	21·03	1·52	6·52	0·60	99·76

Spodiophyllite.—This new mineral occurs as rough, hexagonal prisms or sometimes as thin, trigonal plates; it is optically uniaxial and

negative. There is a perfect basal cleavage with pearly lustre. Colour, ash-grey; very brittle; sp. gr. 2·633. Formula



The mineral resembles the micas and chlorites in its physical characters, but differs from them in containing no water; it is a metasilicate related in composition to ægirite and arfvedsonite. Analysis:

SiO ₂ .	Fe ₂ O ₃ .	Al ₂ O ₃ .	FeO.	MnO.	MgO.	Na ₂ O.	K ₂ O.	Total.
53·61	11·24	4·27	4·13	0·64	10·16	8·55	7·80	100·40

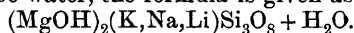
Catapleite.—Three types of crystals are distinguished: the one analysed when considered as hexagonal has [$a:c=1:1\cdot3509$]. Basal sections are in part uniaxial and in part biaxial with $2E=30^\circ$. When a crystal of this type is heated to 30° , or even when held in the warm hand, the twin lamellæ seen in a basal section disappear, and the whole becomes optically uniaxial. It has the usual formula, $Na_2SiO_3, H_4Zr(SiO_4)_2$. Analysis:

SiO ₂ .	ZrO ₂ .	FeO.	Na ₂ O.	H ₂ O.	Total.	Sp. gr.
44·70	30·85	0·71	14·09	9·07	99·38	2·781

Polyolithionite.—This agrees with zinnwaldite in the optical characters and crystal angles, but differs from it in containing more alkalis and silica. Sp. gr., 2·701. Formula, $(Al,Fe)_4(Li_2,K_2,Na_2)_7F_2Si_{16}O_{45}$. The mineral from Narsarsuk contains more potassium and less sodium than Lorenzen's original polyolithionite from the neighbouring locality, Kangerdluarsuk (Abstr., 1886, 677). Analysis:

SiO ₂ .	Al ₂ O ₃ .	Fe ₂ O ₃ .	MnO.	Li ₂ O.	K ₂ O.	Na ₂ O.	F.	Total, less O for F.
58·68	10·24	4·02	0·31	8·24	11·05	1·61	8·16	98·87

Tainiolite.—This new mineral is a member of the mica group; it has the form of strips or bands and so differs in habit from other micas. The colourless crystals are monoclinic, with angles very near those of biotite. There is a perfect basal cleavage; it is optically biaxial and negative; $2E=50^\circ$; sp. gr., 2·86. Assuming the deficiency in the analysis to be water, the formula is given as



This composition distinguishes tainiolite from all other micas.

SiO ₂ .	Al ₂ O ₃ .	FeO.	MgO.	K ₂ O.	Na ₂ O.	Li ₂ O.	Total.
52·2	2·7	0·6	19·1	11·5	1·8	3·8	91·3

Lorenzenite.—The small, acicular crystals of this new mineral are orthorhombic [$a:b:c=0\cdot6042:1:0\cdot3592$]. They have a high adamantine lustre, and are colourless to brownish, with sometimes black ends, they then resemble lucifer matches in appearance; sp. gr., 3·42. Formula, $Na_2(TiO)_2Si_2O_7$. Analysis:

SiO ₂ .	TiO ₂ .	ZrO ₂ .	Na ₂ O.	K ₂ O.	H ₂ O.	Total.
34·26	35·15	11·92	17·12	0·37	0·77	99·59

Leucospheinite.—The white crystals of this new mineral are monoclinic, with a prismatic habit and wedge-shaped terminations [$a:b:c=0\cdot5813:1:0\cdot8501$; $\beta=93^\circ23'$]. Sp. gr., 3·05. Formula, $BaNa_4(TiO)_2(Si_2O_5)_5$. Like petalite, this is a dimetasilicate. The

mineral shows certain crystallographic and chemical relations to eudidymite ($\text{BeSiO}_3, \text{HNaSi}_2\text{O}_6$). Analysis :

SiO_2 .	TiO_2 .	ZrO_2 .	BaO .	Na_2O .	K_2O .	H_2O .	Total.
56.94	13.20	3.50	13.75	11.14	0.56	0.31	99.40

Elpidite.—This is very abundant at Narsarsuk, but it is usually much altered and has the appearance of sticks of decayed wood. Fresh, clear, and transparent crystals are very rare; these give $[a:b:c=0.51008:1:0.97813]$. The material analysed by Lindstrom (Abstr., 1895, ii, 401) was not fresh, and the whole of the water is probably due to alteration, in which case the formula of the mineral would be $\text{Na}_2\text{Si}_2\text{O}_5, \text{Zr}(\text{Si}_2\text{O}_5)_2$.

Narsarsukite.—This new mineral occurs plentifully at Narsarsuk as tabular or cube-shaped, tetragonal crystals with $[a:c=1:0.52352]$. They are honey-yellow, and have a perfect prismatic cleavage. Sp. gr. 2.751. Formula, $12\text{SiO}_2, 2\text{TiO}_2, 3\text{Na}_2\text{O}, \text{FeF}$. Analysis by Christensen :

SiO_2 .	TiO_2 .	Fe_2O_3 .	Al_2O_3 .	MnO .	MgO .	Na_2O .
61.63	14.00	6.30	0.28	0.47	0.24	16.12
		F.	H_2O .	Total less O for F.		
		0.71	0.29	99.74,		

Chalcolamprite.—This is a new member of the pyrochlore group. It is found as small, regular octahedra on crystals of ægirite. The name chalcolamprite alludes to the metallic, coppery lustre on the faces of the crystals. Thin sections of the mineral are translucent, straw-yellow, and isotropic. Sp. gr. 3.77. Formula, $\text{R}''\text{Nb}_2\text{O}_6\text{F}_2 + \text{R}'''\text{SiO}_3$. Analyses: I. Chalcolamprite. II. Endeiolite.

	Nb_2O_5 .	SiO_2 .	TiO_2 .	ZrO_2 .	Ce_2O_3 .	Fe_2O_3 .	MnO .	CaO .	K_2O .
I.	59.65	10.86	0.52	5.71	3.41	1.87	0.44	9.08	0.38
II.	59.93	[11.48]	0.76	3.78	4.43	2.81	0.37	7.89	0.43
		Na_2O .	H_2O .	F. Total less O for F.					
		I.	3.99	1.79	5.06 100.63				
		II.	3.58	4.14	0.69 100.00				

Endeiolite.—This is also a new member of the pyrochlore group; it occurs as small, brown octahedra, which are remarkable in being sometimes twinned on the spinel law. Sp. gr. 3.44. Formula, $\text{R}''\text{Nb}_2\text{O}_6(\text{OH})_2 + \text{R}'''\text{SiO}_3$. Endeiolite differs from chalcolamprite in having hydroxyl in place of fluorine, and both minerals differ from pyrochlore in having $\text{R}'''\text{SiO}_3$ in place of $\text{R}''(\text{Ti}, \text{Th}, \text{Zr})\text{O}_3$. Microlite ($\text{Ca}_2\text{Ta}_2\text{O}_7$) also occurs at Narsarsuk (Abstr., 1895, ii, 401).

Yttrium-apatite.—This forms small, short, hexagonal prisms, which are opaque, with an enamel white colour and a metallic lustre on the surface. Sp. gr. 3.24. The results of the analysis agree with those required for the apatite formula, but part of the lime is replaced by rare earths. The insoluble portion consists of ægirite and neptunite.

P ₂ O ₅ .	CaO.	Y ₂ O ₃ , &c.	Ce ₂ O ₃ , &c.	MgO.	MnO, FeO.	H ₂ O.
41·12	47·67	3·36	1·52	0·79	traces	0·22
		F.	Insol.	Total less O for F.		
		3·59	2·63	99·37		

Another type of apatite occurring as clear, colourless, hexagonal prisms also contains rare earths.

Detailed descriptions are given of the crystallographic and optical characters and modes of occurrence of each of the above minerals, and also of epididymite, eudidymite, ægirite, arfvedsonite, eudialyte, neptunite, &c. The paper is illustrated by nine plates. L. J. S.

Britholite, a New Mineral. By CHR. WINTHER (*Meddelelser om Grönland*, 1899 [1900], 24, 190—196).—This is found in the pegmatites in the nepheline-syenite at Naujakasik, near Julianehaab, Greenland. The opaque, brown crystals are apparently hexagonal prisms with pyramids, but really consist of biaxial orthorhombic individuals twinned together as in aragonite; [$a : b : c = 0·620 : 1 : 0·423$]. $H = 5\frac{1}{2}$; sp. gr. 4·446. Formula,



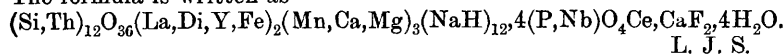
Analysis by C. Christensen :

SiO ₂ .	P ₂ O ₅ .	(Ce, La, Di) ₂ O ₃ .	Fe ₂ O ₃ .	CaO.	MgO.	Na ₂ O.
16·77	6·48	60·54	0·43	11·28	0·13	1·85
		H ₂ O.	F.	Total.		
		1·27	1·33	100·08		L. J. S.

Steenstrupine. By O. B. BOEGGILD (*Meddelelser om Grönland*, 1899 [1900], 24, 203—213).—Besides on the Frith of Kangerdluarsuk, steenstrupine has now been found at other localities in the nepheline-syenite district about Julianehaab, Greenland. The mineral usually occurs as isolated crystals, of which three types are distinguished. Crystals from one of the new localities, namely Tutop Agdlerkofia, are of a different type from those analysed by Blomstrand (*Abstr.*, 1898, ii, 296); they are brownish-black, contain fewer enclosures, and are less altered; the birefringence and dichroism are uniform throughout each crystal; streak colourless; sp. gr. 3·5122; analysis by C. Christensen gave :

SiO ₂ .	Nb ₂ O ₅ .	P ₂ O ₅ .	ThO ₂ .	(Ce, La, Di) ₂ O ₃ .	Y ₂ O ₃ .	Fe ₂ O ₃ .
26·72	4·37	8·19	2·13	29·60	0·36	2·67
						Total
MnO.	CaO.	MgO.	Na ₂ O.	H ₂ O.	F.	less O for F.
6·60	2·33	0·31	11·23	3·45	1·24	98·68

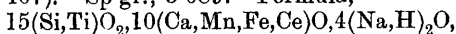
The formula is written as



L. J. S.

Schizolite, a New Mineral. By CHR. WINTHER (*Meddelelser om Grönland*, 1899 [1900], 24, 196—203).—This is found as pink prisms or radiated groups in granular albite, and also rarely in pegmatite, in the nepheline-syenite near Julianehaab, Greenland. The habit, cleavage

and axial ratios [$a:b:c = 1.1496:1:1.0343$; $\beta = 85^\circ 32'$] of the monoclinic crystals closely resemble those of pectolite, of which the mineral may be considered to be a manganese variety, like manganopectolite (Abstr., 1891, 407). Sp gr., 3.089. Formula,



from analysis I, by C. Christensen; the formula of pectolite being $3\text{SiO}_2, 2\text{CaO}, (\text{Na,H})_2\text{O}$.

	SiO ₂ .	TiO ₂ .	Ce ₂ O ₃ .	Y ₂ O ₃ .	FeO.	MnO.	CaO.	MgO.	Na ₂ O.	H ₂ O.	Total.
I.	51.06	0.68	1.47	—	2.79	12.90	19.48	—	10.71	1.36	100.45
II.	51.44	—	—	2.40	2.01	11.69	20.53	0.13	9.50	2.25	99.95

A variety of schizolite occurs in pegmatite at another locality near Julianehaab as very small and indistinct cube-like crystals and plates. Sp. gr., 3.084. Formula, $3\text{SiO}_2, 2(\text{Ca,Mn,Fe,Mg,Y})\text{O}, (\text{Na,H})_2\text{O}$, from analysis II, by C. Christensen. L. J. S.

Action of Ammonium Chloride on Natrolite, Scolecite, Prehnite, and Pectolite. By FRANK W. CLARKE and GEORGE STEIGER (*Amer. J. Sci.*, 1900, [iv], 9, 345—351. Compare this vol., ii, 24, 219).—Natrolite (from Bergen Hill, New Jersey, anal. I) and scolecite (from Whale Cove, Grand Manan Island, New Brunswick, anal. II) when heated at 350° with ammonium chloride in a sealed tube, both give the product $(\text{NH}_4)_2\text{Al}_2\text{Si}_3\text{O}_{10}$. No soluble silica is liberated when the original minerals or this ammonium natrolite are ignited. The formulæ of natrolite and scolecite are therefore written as $\text{Na}_2\text{Al}_2\text{Si}_3\text{O}_{10} + 2\text{H}_2\text{O}$ and $\text{CaAl}_2\text{Si}_3\text{O}_{10} + 3\text{H}_2\text{O}$ respectively, by which they are represented as salts of the acid $\text{H}_8\text{Si}_3\text{O}_{10}$.

Prehnite (from Paterson, New Jersey, anal. III) behaves quite differently, ammonium chloride having very little action at 350° ; very little soluble silica is liberated on ignition. These results support the orthosilicate formula $\text{H}_2\text{Ca}_2\text{Al}_2(\text{SiO}_4)_3$ for prehnite.

Further experiments made on pectolite (this vol., ii, 24) do not lead to any definite results; the ammonium chloride reaction varies in different experiments and is never complete.

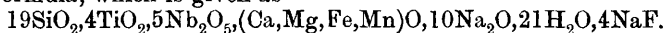
	SiO ₂ .	Al ₂ O ₃ .	Fe ₂ O ₃ .	CaO.	Na ₂ O.	H ₂ O at 100°	H ₂ O above 100°.	Total.
I.	46.62	26.04	—	1.48	15.69	0.39	10.18	100.38
II.	45.86	25.78	—	13.92	0.41	0.40	13.65	100.02
III.	42.31	19.95	6.20	26.63	—	5.02		100.11

L. J. S.

Epistolite, a New Mineral. By O. B. BOEGGILD (*Meddeleser om Grønland*, 1899, [1900], 24, 183—190).—Epistolite was found as large, thin, rectangular plates in pegmatite veins and in granular albite at four localities in the nepheline-syenite region about Julianehaab, S. Greenland. Crystals are rare; they are monoclinic with approximately [$a:b:c = 0.803:1:1.206$; $\beta = 74^\circ 45'$]. The colour is greyish or brownish, but on the perfect basal cleavage it is silver-white, with a strong pearly lustre, $H = 1-1\frac{1}{2}$, very brittle; sp. gr. 2.885. Analysis by C. Christensen gave:

SiO ₂ .	Nb ₂ O ₅ .	TiO ₂	FeO.	MnO.	CaO.	MgO.
27.59	33.56	7.22	0.20	0.30	0.77	0.13
	Na ₂ O.	H ₂ O.	F.	Total less O for F.		
	17.59	11.01	1.98	99.52		

There is also a trace of potassium, but no tantalum or zirconium; 1.75 per cent. of the water is lost below 100°, and is omitted from the formula, which is given as



Epistolite contains more niobium than any other silicate. L. J. S.

Meteorite from Quesa, Spain. By EDUARDO BOSCA Y CASANOVES (*Actas Soc. Española Hist. Nat.*, 1899, 53—56).—This iron fell at Quesa, in Valencia, on August 1st, 1898; it weighs 10670 grams, and has the fine grained structure of an ataxite (compare following abstract). Sp. gr. 6.48. Analyses by Peset gave I for the oxidised outer portion, and II for the interior of the mass.

	Fe.	Ni.	Co, Mn, &c.	O.	Total.
I.	79.07	17.95	traces	2.98	100.00
II.	81.35	18.35	0.30	—	100.00

L. J. S.

Meteoric Iron from Quesa, Spain. By EMIL W. COHEN (*Mitth. naturwiss. ver. f. Neu-Vorpommern Rügen, Berlin*, 1900, 31, 63—66. Compare preceding abstract).—A new examination of a larger piece of this iron shows the structure to be octahedral with lamellæ of medium width. A new analysis (I) has been made, since the previous analysis by Peset shows much more nickel than any other known octahedrite. The previous determination of the fine-grained structure was based on the examination of small fragments from the external part of the mass; this is much poorer in nickel (anal. II) than the interior.

	Fe.	Ni + Co.	P.	Total.
I.	88.73	10.85	0.15	99.73
II.	95.56	4.40	—	99.96

L. J. S.

Gases Evolved by the Springs of Mont-Dore. By F. PARMENTIER and A. HURION (*Compt. rend.*, 1900, 130, 1190—1191).—The gas evolved by the spring water of Mont-Dore has the following percentage composition: Carbon dioxide, 99.50; nitrogen, 0.49; argon, 0.01.

H. R. LE S.

Combustible Gases of Salsomaggiore. By RAFFAELE NASINI and ROBERTO SALVADORI (*Gazzetta*, 1900, 30, i, 281—296).—Analyses are given of the various gases which are evolved, together with the saline waters and petroleum, from the springs of Salsomaggiore. The gases, which burn with a luminosity about equal to that of ordinary coal gas, consist for the most part of methane and ethane, with varying and, in general, small proportions of unsaturated hydrocarbons, nitrogen and carbon dioxide.

T. H. P.

Physiological Chemistry.

The Percentage Oxygen Capacity and Total Oxygen Capacity and the Total Mass of Blood in Man. By JOHN S. HALDANE and J. LORRAIN SMITH (*Proc. Physiol. Soc.*, 1900, v—vi; *J. Physiol.*, 25).—The oxygen capacity of the hæmoglobin in ox-blood was first determined by the ferricyanide method. A small volume of human blood was then compared colorimetrically with the ox-blood, and its percentage oxygen capacity calculated, for the colour of the blood runs parallel to its power of absorbing oxygen. In healthy human blood, the percentage oxygen capacity is between 16 and 21. The total oxygen capacity was determined by allowing the subject of the experiment to breathe and absorb a known volume of carbon monoxide. The percentage saturation of the hæmoglobin was determined in a drop of the blood by the carmine method, and from the result the total capacity of the blood for absorbing carbon monoxide or oxygen could easily be calculated. The total volume of the blood was then calculated from the two preceding numbers, and its mass by multiplying the volume by the specific gravity. The commonly accepted estimate that the weight of the blood is equal to about a twelfth of the body weight is much too high; the average amount is only a twentieth of the body weight. W. D. H.

The Volume, Total Oxygen Capacity, and Percentage Oxygen Capacity of the Blood in Chlorosis and Pernicious Anæmia. By J. LORRAIN SMITH (*Proc. Physiol. Soc.*, 1900, vi—vii; *J. Physiol.*, 25).—In chlorosis, the total oxygen capacity is approximately normal, but the percentage oxygen capacity is markedly diminished (often below 50 per cent.); the volume of the blood is markedly increased. The decrease in the number of red corpuscles and in the amount of hæmoglobin cannot be regarded as due simply to increase in the plasma. In pernicious anæmia, both percentage and total oxygen capacity are greatly diminished, but the volume of the blood is increased. The decrease in the number of the red corpuscles, and in the amount of hæmoglobin, is greater than can be explained by the increase in the volume of the blood. W. D. H.

Relationship of Iron to Blood-formation. By EMIL ABDERHALDEN (*Zeit. Biol.*, 1900, 39, 487—523).—Previous portions of the research have shown that inorganic iron, hæmoglobin, and hæmatin in the food are absorbed, and lead to an increase of body weight, and of the blood-pigment. The most important fact now added is that animals on their normal diet assimilate more iron than those kept on a diet poor in iron, to which inorganic iron salts, hæmoglobin, or hæmatin has been added. W. D. H.

Effect of Ingestion of Alcohol on the Blood of Mother and Foetus, and on the Milk. By MAURICE NICLOUX (*Compt. rend.*, 1900, 130, 855—858).—Experiments were made on dog, sheep, and guinea-pig. Ingested alcohol passes into the milk. The amounts of

alcohol in the blood and milk of the mother and the blood of the foetus are approximately equal. W. D. H.

Chemical Changes in the Blood produced by Feeding with Ammonium Sulphate. By THEODOR RUMPF and O. SCHUMM (*Zeit. physiol. Chem.*, 1900, 29, 249—255).—After the administration of ammonium sulphate, the amount of alkali in the blood is diminished; this is chiefly due to a lessening of organic sodium compounds. The sodium chloride and the amount of calcium in the blood are increased; the water is lessened. W. D. H.

Hæmorrhage and Transfusion in Dogs. By PERCY M. DAWSON (*Amer. J. Physiol.*, 1900, 4, 1—24).—A full account of experiments concerning which a preliminary communication has already been made (this vol., ii, 291). An important new point is that transfusion of Ringer's fluid containing more than 0.026 per cent. of calcium chloride is dangerous. More than this appears to over-stimulate the heart; and several cases of death in dogs occurred. W. D. H.

Gaseous Metabolism of the Submaxillary Gland. By JOSEPH BARCROFT (*J. Physiol.*, 1900, 25, 265—282).—This preliminary paper treats mainly of methods. The form of gas pump used is described in full with illustrations; it is a modification of Tœpler's. Haldane's method of gas analysis was employed. Incoagulability of the blood is best brought about in dogs, which were the animals used, by injection of leech extract: this is not absolutely certain to produce incoagulability, but it has the advantage of not influencing the flow of saliva. The amount of oxygen and carbon dioxide in the blood is, however, increased. The anæsthetics found most suitable were morphine and chloroform; the effect of these anæsthetics on the blood gases is inconstant, but the most marked feature is a gradual increase in the carbon dioxide. W. D. H.

Influence of Asparagine and Ammonia on Proteid Metabolism in Ruminants. By OSCAR KELLNER, A. KÖHLER, F. BARNSTEIN, W. ZIELSTORFF, R. EWERT, and K. WEDEMEYER (*Zeit. Biol.*, 1900, 39, 313—376).—The experiments recorded with full details were performed on four sheep. In two, the amount of proteid in the food was small, in the other two, medium. In the first case, the addition of asparagine furthers the putting on of proteid; ammonium acetate has the same action. In the second case, asparagine has no action in influencing either the digestion or the assimilation of proteid. W. D. H.

Nuclein Metabolism. By OTTO LOEWI (*Chem. Centr.*, 1900, i, 871; from *Arch. exp. Path. Pharm.*, 44, 1—23).—The quantity of phosphoric and uric acids in the urine largely depends on the amount of nuclein in the food. Allantoin does not occur. After feeding on allantoin, only a small amount of it is found in the urine. W. D. H.

Energy-value of Flesh and Proteids. By EDOUARD PFLÜGER (*Pflüger's Archiv*, 1900, 79, 537—596).—The article is mainly a

critical review of our knowledge of the subject, and the numerous errors which must be avoided in a study of the metabolism of proteid material. Considerable space is devoted to a criticism of Rübner's methods and results. The urine, after flesh diet, receives contributions from the metabolism of fat, and cannot be considered a purely 'flesh urine.' Rübner's assumption that meat extract takes no part in metabolism is questioned, at any rate in regard to those extractives which do not pass unchanged into the urine. W. D. H.

Influence of Alcohol on Muscular Work. By J. C. TH. SCHEFFER (*Chem. Centr.*, 1900, i, 870—871; from *Arch. exp. Path. Pharm.*, 44, 24—58).—From experiments made with Mosso's ergograph, it appears that alcohol causes first an increase of muscular work, and later a decrease. The irritability passes through corresponding phases. If the peripheral motor nerve apparatus is eliminated in animals by curare, alcohol has no effect. W. D. H.

Transformation of Fat into Glycogen. By CHARLES BOUCHARD and ALEXANDRE DESGREZ (*Compt. rend.*, 1900, 130, 816—822).—In a starving animal, the copious administration of fat does not increase the glycogen of the liver, but there is a rise in that of the muscles. Fat is therefore regarded as one source of the muscular glycogen; another source is the sugar of the blood that leaves the liver. On oxidation, muscular glycogen is stated to pass into the condition of lactic acid, and not into that of sugar. W. D. H.

Action of Soaps in the Body. By IMMANUEL MUNK (*Chem. Centr.*, 1900, i, 676; from *Centr. Physiol.*, 13, 657—661).—When soaps are introduced into the blood, the heart is affected, and the blood pressure sinks. In the case of sodium soaps, Bottazzi (*Arch. Ital. Biol.*, 32, 176) attributes this action to the sodium. This cannot be the case, since to produce such a fall of pressure a quantity of sodium hydroxide is necessary much larger than that which can be formed by dissociation from the soap injected. W. D. H.

Absorption of Fats and Soaps in the Large Intestine. By HARTOG J. HAMBURGER (*Archiv Anat. Physiol. Physiol. Abth.*, 1900, 433—464).—The experiments on dogs which are here recorded show that the large intestine is capable of absorbing fats, this property not being confined, as hitherto thought, to the small intestine. In order to obtain marked absorption, it is necessary to take an emulsion and leave it a long time in the intestine. Admixture with sodium carbonate is unnecessary; sodium chloride, which is rapidly absorbed, will do as well. Admixture with *sapo medicatus* also suffices. Soaps are absorbed, but during absorption are partly converted into fats. This is brought about by the mucous membrane; it can be proved after the removal of the intestine from the body, and is also brought about by the 'surviving' membrane after it is finely minced. Heating the mucous membrane to 80° destroys this property. W. D. H.

Fixation of Alkaline Bases in the Foetal Body during the last Five Months of Intrauterine Life By LOUIS HUGOUNENQ (*Compt. rend.*, 1900, 130, 941—942).—The proportion of potassium

and sodium in the ash of fœtuses of different ages was determined. As growth takes place, both bases increase in amount, but the sodium increases more rapidly on account of the richness of cartilage in sodium chloride. The potassium is a predominant element of red blood corpuscles, and in well nourished subjects increases more rapidly than in the cases of malnutrition. W. D. H.

Absorption of Iodides by the Skin. By F. GALLARD (*Compt. rend.*, 1900, 130, 858—861. Compare Abstr., 1899, ii, 503).—The skin of man and animals can absorb aqueous solutions of iodides. The elimination by the urine is slow, so that some accumulation occurs in the tissues. The respiratory mucous membrane only permits the entrance of a very small amount of iodine. W. D. H.

Variations of the Iodine of the Thyroid of New Born Children under various Pathological Influences. By ALBERT CHARRIN and BOURCET (*Compt. rend.*, 1900, 130, 945—948).—In various cachectic conditions of the mother, the new born child is feeble, and often suffers no harm from injections of thyroid extract. There are frequently histological changes in the thyroid of these infants. The present paper records the examination of the thyroid in 32 cases of the kind. In 18 of these, no iodine was found; the maladies of the mother and the child were very different. In the remaining 14 cases, the pathological conditions being here equally variable, the percentage of iodine in the dry gland varied from 0.001 to 0.006. W. D. H.

Hüfner's Method of preparing Pure Glycocholic Acid. By W. A. OSBORNE (*Proc. Physiol. Soc.*, 1900, xi—xii; *J. Physiol.*, 25).—Hüfner (*J. prakt. Chem.* [ii], 1874, 10, and 1879, 19) described an effective method of obtaining glycocholic acid from ox-bile. The main points in the method are that bile is shaken up with ether and hydrochloric acid. In a short time, crystals of glycocholic acid separate out so abundantly as to render the bile almost solid, and may be purified by washing and recrystallisation. Certain observers have cast doubt on the method, and in some districts of Germany success was generally not obtained. In America, also, the separation of the crystals occurred in only 22 per cent. of the specimens of ox-bile examined. The present paper shows that the bile of English oxen and cows gives completely successful results. The method also succeeds with rabbits' bile. W. D. H.

The Maximum Production of Hippuric Acid in Rabbits. By F. H. PARKER and GRAHAM LUSK (*Amer. J. Physiol.*, 1900, 3, 472—484. Compare Abstr., 1899, ii, 312).—In a fasting rabbit fed with lithium benzoate, the amount of glycocine eliminated as hippuric acid in the urine indicates that 4 grams may be derived from the metabolism of every 100 grams of body proteid, and the excretion runs parallel to the proteid destroyed. Administration of carbohydrates has no effect. After gelatin, the number sinks to 3.1 from the combined metabolism of gelatin and proteid; after casein, it is 3.45. After phloridzin and benzoic acid in one experiment, the number was doubled, but this could not be repeated. In metabolism the proteid

and gelatin molecule may yield glycocine to the amount of at least 3 to 4 per cent. W. D. H.

Caseinogen of Human Milk. By ERWIN KOBRAK (*Pflüger's Archiv*, 1900, 80, 69—85).—The caseinogen was prepared from centrifugalised milk by the careful addition of acetic acid; various foreign substances were then removed by dialysis, and the product purified by means of alcohol and ether. It differs from the caseinogen of cows' milk, especially in its small degree of acidity; the casein formed from it by rennet is flocculent, not coherent. By repeated solution in alkali and precipitation by acid, a product is finally obtained, practically identical with cow-caseinogen. Human caseinogen is therefore probably a nucleo-proteid identical with that obtained from cows' milk, but containing an admixture of some basic, proteid-like material, possibly histon or protamine. W. D. H.

[**Glycolytic Action of the Pancreas and of Urine.**] By G. PIERALLINI (*Chem. Centr.*, 1900, i, 828; from *Zeit. Klin. Med.*, 39, 26—31).—The urine, both in health and disease, has no glycolytic action. Search for a glycolytic ferment in the human pancreas removed after death gave uncertain results. W. D. H.

Lipolytic Ferment in Human Ascitic Fluid. By HARTOG J. HAMBURGER (*Proc. K. Akad. Wetensch. Amsterdam*, 1900, 2, 428—436).—It is extremely probable that the lymph contains an agent which reduces the fat emulsion of the intestine to the extremely finely divided condition in which it is found as the 'molecular basis' of chyle. As the lymph of the villi is difficult to collect in quantity, advantage was taken of a case of ascitic fluid, supposed to be chylous. The opalescent character of this fluid was, however, found not to be due to fat, but to mucoid; nevertheless, it was found possible to make with this fluid, as well as with ordinary horse serum, a perfect "dust-like" emulsion. Possibly the continual movement of the lymph in the villi normally produces a like change. The same ascitic fluid contains also a lipolytic ferment, which acts on the finely divided fat; but for this action, the presence of blood corpuscles and access of air are also necessary. The ferment is a constituent of the chyle rather than of the blood, as Cohnstein and Michaelis consider. W. D. H.

A Diastatic Ferment in Hen's Eggs. By JOHANNES MÜLLER and M. MASUYAMA (*Zeit. Biol.*, 1900, 39, 542—559).—The yolk of the hen's egg contains, in not unimportant quantities, an enzyme, which is capable of transforming starch into dextrin and sugar (*isomaltose*). W. D. H.

Meningocele Fluid. By WLADIMIR VON GULEWITSCH (*Zeit. physiol. Chem.*, 1900, 29, 281—282).—Choline was sought for in a specimen of cerebro-spinal fluid removed from a meningocele, with negative results. This confirms the statement made by Mott and Halliburton (*Abstr.*, 1899, ii, 315) that normal cerebro-spinal fluid does not contain this base. W. D. H.

The Crystalline Stalk of Acephalous Molluscs. By HENRI COUPIN (*Compt. rend.*, 1900, 130, 1214—1216).—The crystalline stalk

of acephalous molluscs has been regarded as a copulative organ, and as a manubrium to agitate the gastric contents. The present research, carried out on *Cardium edule*, shows that the weight of the organ is 0.03 gram, and it contains 87 per cent. of water. It is regarded as a digestive agent containing the ferments amylase with a little sucrase.

W. D. H.

Solution of Uric Acid by means of Nucleic Acid. By ALBRECHT KOSSEL and GOTO (*Sitzungber. Ges. gesammt. Naturwissensch. Marburg*, 1900, April 6).—It has been previously shown that nucleic acid will unite with certain quantities of purine bases. The present research shows that similar loose combinations are formed between nucleic acid and thymic acid on the one hand, and uric acid on the other, and in this way more uric acid is dissolved than in control specimens where the nucleic acid is absent. It is thus possible that the action of nucleic acid and its compounds in the body may be a factor in determining the solubility of uric acid there. Whether nucleic acid can be used as a therapeutic agent in assisting the solution of uric acid is another possibility.

W. D. H.

Investigation of Urine by a Combination of the Freezing Point and Blood Corpuscle Methods. By HARTOG J. HAMBURGER (*Centr. inn. Med.*, 1900, No. 12).—A combination of the two methods mentioned above affords a means of determining approximately the osmotic pressure due to inorganic constituents (such as sodium chloride) and organic constituents (such as urea). If Δ be determined for the urine, and then, by means of the blood corpuscle method, the osmotic pressure is found equal to that of a saline solution of a certain strength, of which the depression of freezing point is Δ , then $\Delta - \Delta'$ gives the value to be assigned to urea and similar substances. Examples are given and the question discussed from the theoretical standpoint.

W. D. H.

Glycuronic Acid in Normal Urine. By PAUL MAYER and CARL NEUBERG (*Zeit. physiol. Chem.*, 1900, 29, 256—273).—The work recorded covers much the same ground as that in a paper previously published (this vol., ii, 155). The following additional fact of physiological importance is added, that glycuronic acid compounds are constituents of normal urine; the greatest part of the acid is combined with phenol, and smaller amounts with indoxyl and scatoxyl.

W. D. H.

Elimination of Nitrogen, Sulphates, and Phosphates after Ingestion of Proteid Food. By H. C. SHERMAN and P. B. HAWK (*Amer. J. Physiol.*, 1900, 4, 25—49).—The experiments were conducted by the authors on themselves. The urine was collected at three hour intervals; the rates of excretion of nitrogen and sulphates run closely parallel, and show a tendency to rise during the morning, reaching a maximum after the midday meal, with a slight fall in the following period, and another rise after the evening meal. A minimum is reached during the night. The excretion of phosphates describes a different curve, rising steadily from the middle of the morning until retiring, falling during sleep and continuing to fall for three hours

after rising, reaching a minimum after breakfast. When 64 grams of extra proteid was taken with breakfast, the output of nitrogen began to rise three hours later until the sixth to the ninth hour, when it declined at first rapidly, and then slowly, until it reached the normal in about 36 to 39 hours. The excretion of sulphates runs a similar course; the rise, however, begins a little later, and reaches the normal a little earlier. The increase in the rate of excretion of phosphates begins a little later still, reaches a maximum simultaneously with the nitrogen, and then regains the normal very rapidly in from 12 to 15 hours.

The increased heat of combustion of the urine was but little greater than would correspond with an amount of urea equivalent to the extra nitrogen eliminated. This indicates that the amount of less highly oxidised constituents of the urine was but little affected. The nature and extent of the changes in the urine seem to have been about the same when the proteid was simply added to the diet as when it was substituted for an isodynamic amount of fat. A moderate gain or loss of body nitrogen does not affect the changes noted. W. D. H.

Indicanuria Produced by Administration of Oxalates. By ERICH HARNACK and ELSE VON DER LEYEN (*Zeit. physiol. Chem.*, 1900, 29, 205—221).—Indicanuria can be produced by poisoning with dilute sulphuric acid (2.5 to 6 per cent. solution), but much more readily and intensely by the administration of oxalic acid by the mouth or subcutaneously. In order to produce this effect, the best form to give is sodium oxalate, and non-toxic doses will accomplish the result; for instance, in a large dog, 0.06 gram given subcutaneously is enough. The indigotin does not apparently arise in the alimentary canal, but as a result of disordered tissue metabolism. W. D. H.

Comparative Investigation of the Fæces after Feeding on Meat and Plasmon. By KARL MICKO (*Zeit. Biol.*, 1900, 39, 430—450).—After feeding on plasmon, the fæces contain no unabsorbed proteids; absorption is stated to be even more complete than after a meat diet. W. D. H.

Organic Phosphorus in Fæces after Feeding on Milk. By PAUL MÜLLER (*Zeit. Biol.*, 1900, 39, 451—481).—By examining the fæces of children fed, some on human, some on cow's milk, no difference between them could be discovered. The N:P ratio was determined by two methods; but the results were practically identical in all cases. The statement made by Knopfmacher, that after feeding on cow's milk there is a considerable digestion residue rich in phosphorus in the fæces, was, therefore, not confirmed. W. D. H.

Composition of Urinary Calculi. By LEOPOLD SPIEGEL (*Chem. Centr.*, 1900, 1, 616—617; from *Ber. deutsch. pharm. Ges.*, 9, 318—326).—A large number of analyses of stones removed from various parts of the urinary tract are recorded. W. D. H.

Secretion of Pepsin in Gastric Disease. By ROTH (*Chem. Centr.*, 1900, i, 618; from *Zeit. klin. Med.*, 39, 1—12).—Mett's method (*Diss.*, Petersburg, 1899) is recommended for the clinical estimation of

pepsin in the stomach contents. From a consideration of numerous cases of disease, the estimation of pepsin is considered to have less value for diagnostic than for therapeutic purposes. W. D. H.

[Metabolism in Leucæmia.] By C. VON STEJSKAL and F. ERBEN (*Chem. Centr.*, 1900, i, 828—829; from *Zeit. klin. Med.*, 39, 151—170).—These are chiefly studies in metabolism in various forms of leucæmia. W. D. H.

Physiological Effects of Extracts of Nervous Tissues. By WILLIAM D. HALLIBURTON (*Proc. physiol. Soc.*, 1900, vii—ix; *J. Physiol.*, 25).—Saline extracts of various nervous tissues (fresh and dried) produce a temporary fall of blood pressure, partly by their effect on the heart, partly by causing a dilatation of splanchnic blood vessels. The effect is more marked the greater the proportion of grey matter in the tissue used. The effect is not abolished by section of both vagi, nor, as a rule, by the administration of atropine. The depressor substance is soluble in alcohol, and choline is always to be found in the alcoholic solution. Possibly lactic acid and other substances not yet identified are partly responsible for the effect; these substances will account for the fact that the effect is not always completely neutralised by atropine. It is not advisable to employ glycerol extracts, for glycerol itself has a depressor action. W. D. H.

Physiological Effects of Extracts of Nervous Tissues. By W. A. OSBORNE and SWALE VINCENT (*J. Physiol.*, 1900, 25, 283—294; *Proc. physiol. Soc.*, 1900, ix—x; *J. Physiol.*, 25).—The main results are the same as those recorded in the preceding abstract. The principal difference is the following: although choline is admittedly present in the extracts, its amount is not regarded as sufficient to account for the effect produced, and it is moreover stated that the depressor effect of the extracts is not abolished by atropine. The other substance or substances responsible for the fall of blood pressure were not identified; they are soluble in alcohol and in ether. W. D. H.

Anti-leucocytic Serum; its Action on the Coagulation of Blood. By C. DELEZENNE (*Compt. rend.*, 1900, 130, 938—940).—Certain products of bacterial agency in the blood-serum are believed to hinder coagulation by causing destruction of the leucocytes. Peptone is believed to act in a similar way. The anti-coagulating action of such serum can only be demonstrated by injecting it into the blood stream; *in vitro*, it accelerates coagulation. W. D. H.

Chemical Behaviour of Drugs and Poisons in the Organism. By SIGMUND FRÄNKEL (*Chem. Centr.*, 1900, i, 775—776; from *Pharm. Post*, 33, 109—111).—A discussion on general pharmacological questions, and of the work of others on the subject. W. D. H.

Action of some Aliphatic Compounds. By MÅRTEN ELFSTRAND (*Chem. Centr.*, 1900, i, 560; from *Arch. exp. Path. Pharm.*, 43, 435—455).—Valeraldehyde, pentane, and cyclopentadiene are narcotics like ether, but are not as powerful; cyclopentadiene acts also on muscles,

causing rigor. During the narcosis produced, stimulation of the vagus causes no inhibition of the heart.

W. D. H.

Physiological Action of Nitriles. By EDMOND FIQUET (*Compt. rend.*, 1900, 130, 942—945).—Acetonitrile is less toxic than generally supposed. In rabbits and guinea-pigs, 1.5 c.c. per kilo. of body weight are necessary to cause death rapidly. The higher nitriles are very toxic, and act like certain ptomaines; they produce loss of sensation and muscular paralysis, preceded by convulsions. Very similar effects follow the injection of urine. The influence of the CO_2H and SO_3H groups is to lessen the toxic power of nitriles.

W. D. H.

Action of Santonin and Amyl Nitrite on Vision. By WILHELM FILEHNE (*Pflüger's Archiv*, 1900, 80, 96—107).—In frogs poisoned by santonin and kept in the dark, no departure from the normal is noted in the retinal pigments; but if the animals are kept in the light, and then placed in darkness, there is little or no regeneration of the visual purple, and the melanin-laden epithelial cells show little activity. Amyl nitrite acts in the same way, except that the epithelial cells behave normally in conditions both of light and darkness.

W. D. H.

Action of Caffeine and Theobromine on the Heart. By JOHANNES BOCK (*Chem. Centr.*, 1900, i, 559; from *Arch. exp. Path. Pharm.*, 43, 367—399).—Both caffeine and theobromine cause the isolated mammalian heart to beat more quickly and lessen its elasticity. With large doses, the blood pressure sinks. In rabbits, small doses of caffeine when injected cause a lessening of the heart's rate; this is the result of stimulation of the vagus centre. The rise of blood pressure is due to stimulation of the vaso-motor centre.

W. D. H.

Physiological Action of 1- and 4-Methylxanthines. By MANFREDI ALBANESE (*Chem. Centr.*, 1900, i, 558—559; from *Arch. exp. Path. Pharm.*, 43, 305—310).—The two methylxanthines produce muscular rigor in frogs. 0.01 gram of heteroxanthine or of 1-methylxanthine is lethal; the same dose of 4-methylxanthine only causes slight stiffness. After the injection of methylxanthine, caffeine and theobromine produce little or no tetanus, as they usually do. The lethal dose of 4-methylxanthine in dogs is from 0.3 to 0.4 gram per kilo. of body weight. Smaller doses cause convulsions and affect the breathing, although the heart is still powerful and regular. Heteroxanthine produces no convulsions, but paralysis. With moderate doses of the two methylxanthines, the frequency of the pulse and the arterial pressure go up; with larger doses, although the pulse is still fast, the pressure goes down. In dogs, these substances cause no diuresis, but in rabbits they do. A small quantity of the methylxanthines appears unchanged in the urine.

W. D. H.

Action of Nicotine on Respiration and Circulation. By HEINRICH WINTERBERG (*Chem. Centr.*, 1900, i, 559—560; from *Arch. exp. Path. Pharm.*, 43, 400—434).—In mice and rabbits, nicotine is very fatal, and produces clonic spasms and cessation of respiration.

Smaller doses stimulate respiration. The blood pressure first sinks and then rises.

W. D. H.

Comparative Action of Veratrine Alkaloids on Muscle and Nerve. By AUGUSTUS D. WALLER (*Proc. Physiol. Soc.*, 1899; *J. Physiol.*, 1900, 25).—A frog poisoned by veratrine has muscles that give the well known protracted contraction and nerves that give normal electrical variations in activity. A frog poisoned by proto-veratrine has muscles that give a normal contraction and nerves that give a protracted negative variation.

W. D. H.

Chemistry of Vegetable Physiology and Agriculture.

Production of Quinone by Streptothrix Chromogena and the Biology of this Microbe. By MARTINUS W. BEIJERINCK (*Arch. Neerl.*, 1900, iii, 2, 327—340).—The organism *Streptothrix chromogena*, which is peculiar on account of its capability of causing the formation of quinone, had been previously known to the author as *S. humifica* on account of its playing an active part in the formation of humus in soil; it is probable that both functions are intimately connected. As probably many species exist, the name *S. chromogena Gasperini* is given to the particular microbe examined, and of this, as well as of an allied species, *S. alba*, descriptions are given. It is a minute myceliform vegetation whose spores possess considerable powers of resistance, withstanding water at 80°, but being destroyed at 100°. It is found in soils to the depth of one or two metres, and is abundant in the soil adhering to roots. The author believes the organism to be important to plant life, not only on account of its rapidly converting nitrates into nitrites, and of producing humus, but also probably in aiding the accomplishment of vital processes of which the roots themselves are incapable. The tests are described by which the presence of quinone or of quinhydrone was determined, and the mode of its formation is discussed. It is probably formed from albumin or peptones, as a consequence of catalytic decompositions due to the organisms.
L. M. J.

Action of Fluorescent Substances on Infusoria. By OSCAR RAAB (*Zeit. Biol.*, 1900, 39, 524—546).—In researches on the action of acridine, phosphines, and eosin, daylight was found to increase the destructive influence on infusoria; this is evidently connected with the fluorescence of these compounds. The rays which act most in this way are those which most excite fluorescence, and it is probable that fluorescent substances are able to transform the energy of rays of light into chemical energy. It is also probable that fluorescence plays a part in the animal organism, but in a lesser degree. W. D. H.

Reactions to Stimuli in Unicellular Organisms. By HERBERT S. JENNINGS (*Amer. J. Physiol.*, 1900, 3, 397—403).—The experiments previously described (this vol., ii, 158) are again discussed, and points

of disagreement with Garrey (*ibid.*) considered. These points are mainly those of nomenclature and interpretation of results.

W. D. H.

Root Nodules of Alder and Elæagnus. By LORENZ HILTNER (*Forstl. naturw. Zeit.*, 1898, 7, 415—423).—It was previously shown (*Landw. Versuchs-Stat.*, 46, 153) that, like the *Leguminosæ*, alder plants when provided with root nodules grow normally in absence of combined nitrogen. Some trees have now been growing for five years in sand without nitrogenous manure, and have attained a height of 1.5 metres. Young alder trees grown in ordinary soil continue to grow normally when planted in sand free from nitrogen.

The organism which produces the nodules, *Frankia subtilis*, forms a connecting link between bacteria and fungi. Unlike leguminous plants, alder plants develop normally in water cultures when the nodules remain covered with water (compare this vol., ii, 299). Nodules which seem to be produced by the same organism occur on all varieties of alder.

As regards *Elæagnus*, inoculated plants have grown for seven years without combined nitrogen. Probably all the varieties, such as *Hippophaë* and *Shepherdia*, are enabled, by symbiosis, to utilise free nitrogen (compare Frank, *Ber. deut. bot. Ges.*, 1891, 9, 224.) N. H. J. M.

Assimilation by Means of Chlorophyll. By GINO POLLACCI (*Chem. Centr.*, 1900, i, 822; from *Atti. Inst. Bot. Pavia*, 7, October, 1899. Compare this vol., ii, 160).—The green organs of plants grown in sunlight restore the colour of magenta which has been decolorised by sulphurous acid, whilst fungi or plants which have been kept for a long time in the dark or in an atmosphere free from carbon dioxide do not give this reaction. The distillate obtained by boiling the liquid expressed from plants which have grown in sunlight shows all the reactions of formaldehyde. E. W. W.

Chlorophyllous Assimilation in Indoor Plants. By ED. GRIFFON (*Compt. rend.*, 1900, 130, 1337—1340).—Plant species in general, whether indigenous or cultivated in hothouses, are quite incapable of decomposing carbon dioxide in dimly-lighted apartments; the minimum intensity of illumination at which chlorophyllous assimilation is possible varies for each species. The respiration of certain plants (heather, *Begonia* and *Selaginella*) is so feeble that it is counter-balanced by assimilation even in diffused daylight, and accordingly these species evolve oxygen when cultivated in partly darkened rooms (compare this vol., ii, 159). G. T. M.

Occurrence of Albumin, Albumose, and Peptone in the Vegetative Portions of Plants. By THOMAS BOKORNY (*Pflüger's Archiv*, 1900, 80, 48—68).—The principal references to the literature of this subject from Ritthausen onwards are given. The chief new point made out in an investigation of the soluble proteids in numerous portions of plants of different kinds is that, with the exception of fungi and seedlings, proteoses and peptone are almost altogether absent. W. D. H.

Occurrence of Dulcitol in the Bark of *Evonymus Artropurpureus*. By M. HOEHNEL (*Chem. Centr.*, 1900, i, 869; from *Pharm. Zeit.*, 45, 210—211).—The bark of *Evonymus artropurpureus* has been found to contain dulcitol, but not mannitol. The dulcitol was isolated and identified by its properties and behaviour. E. W. W.

Gummy Substance in Elm Galls. By NAPOLEONE PASSERINI (*Ricerche Esper. Istituto Agrar. Scandicci*, 1896—1897).—The galls of *Ulmus campestris* contain a dense, syrupy liquid which is colourless or slightly yellowish, or more rarely brown. The liquid is slightly alkaline, does not show the tannin reaction with ferric chloride, and is strongly dextrorotatory. Sp. gr. 1.06553 at 21°. It contains 18.94 per cent. of a gum, precipitated by alcohol, which resembles gum arabic in appearance. The gum does not yield mucic acid with nitric acid, or furfuraldehyde when distilled with hydrochloric acid; and it is not coloured by iodine. It is precipitated by lead acetate, and reduces copper salts readily. When oxidised with nitric acid, much tartaric and very little oxalic acid are formed. N. H. J. M.

Distribution of the Diastatic Enzyme in the Potato Plant. By ADOLF MAYER (*Chem. Centr.*, 1900, i, 823—824; from *J. Landw.*, 48, 67—70).—In order to ascertain the distribution of the diastatic enzyme, the amount of diastase in the following materials was approximately determined. (1) Old germinated potatoes, and (2) the sprouts from these potatoes; (3) old potatoes from the field; (4) the young tubers attached to these; (5) the stalks above the ground, and (6) the leaves on these stalks. (1) and (6) were found to contain by far the most diastase, (2) contained very much less, and (3), (4) and (5) were practically free from diastase. Thus, in accordance with the present theory, the organs from which the carbohydrate is sent throughout the plant are the richest in the diastatic enzyme. The old tubers from the field no longer contained diastase, but in this case, the plant being already completely developed and producing abundance of carbohydrate, a supply from the mother tuber was no longer necessary.

Similar experiments made with sugar beet showed that none of the organs contained any enzyme analogous to invertin. In this case, however, the monosaccharides passing through the leaves are not necessarily formed from sugar, and in fact the roots always contain more sugar than the leaves. Experiments with oats show that the ripe seed contains much larger quantities of the diastatic enzyme than the half-ripe ears. E. W. W.

Formation of Vanillin in Potato Parings and its Detection. By W. BRÄUTIGAM (*Chem. Centr.*, 1900, i, 728; from *Pharm. Zeit.*, 45, 164).—Vanillin does not occur in fresh potato parings, but is formed under the influence of warmth and atmospheric oxygen, its formation not being dependent on any bacteriological process. The amount of vanillin formed depends on the temperature, &c., and also on the kind of potato.

Fresh bark taken from a lime tree in summer was found to contain vanillin, but the bark of the same tree in winter was devoid of this substance. E. W. W.

Products in Tobacco Smoke. By HERMANN THOMS (*Chem. Centr.*, 1900, i, 826—827; from *Ber. Deutsch. Pharm. Ges.*, 10, 19—31).—Experiments on the products in tobacco smoke have led to the following conclusions: (1) Tobacco smoke contains the following bases which are injurious to health: nicotine and its decomposition products, pyridine and homologues, and a peculiar, poisonous, ethereal oil which is only formed during the combustion of the tobacco. (2) A solution of alkali not only extracts carbon dioxide and butyric acid from tobacco smoke, but also hydrocyanic acid. The quantity of the last is too small, however, to exercise any physiological influence. (3) The quantity of carbon monoxide in the smoke is also too small to have any deleterious effect. (4) A cigar end may contain as much as 3—4 times the amount of nicotine originally present in the tobacco. (5) Of the total nicotine contained in the smoke, 75 per cent. was isolated as such, whilst 25 per cent. was decomposed. The original paper contains a sketch of an apparatus by means of which products in the smoke of cigars may be examined, 10—15 cigars being sufficient for the test. The amount of nicotine in the cigars is first determined by Keller's method (*Abstr.*, 1899, ii, 193), or by the author's potassium bismuth iodide method. In the latter, which depends on the property of the iodide of precipitating nicotine and organic bases, but not ammonia, 10 grams of the sliced cigars are left in contact with 100 c.c. of 10 per cent. sulphuric acid in a closed vessel for 24 hours at a moderate temperature; to 50 c.c. of the filtered extract, 10 c.c. of potassium bismuth iodide solution (Kraut, *Abstr.*, 1882, 528) are added, the precipitate collected, washed with a little water, and then treated with 20 c.c. of a 15 per cent. sodium hydroxide solution; the alkaline liquid is shaken with 40 c.c. of a mixture of equal volumes of ether and light petroleum, and to 20 c.c. of this extract 10 c.c. of a mixture of equal volumes of alcohol and water and a drop of iodoeosin solution are added, and the mixture is finally titrated by Keller's method. The percentage of nicotine is found by multiplying the c.c. of decinormal hydrochloric acid used by 0.6480. The pyridine bases are removed by distilling the acetic acid solution in steam, and the nicotine and ammonia left behind are separated by the above method. E. W. W.

Experiments on the Physiological Phenomena which accompany Chlorosis in the Vine. By GEORGES CURTEL (*Compt. rend.*, 1900, 130, 1074—1076).—The effects of chlorosis are (1) a decided weakening of respiratory activity resulting in a diminution of the relation CO_2/O_2 , (2) a diminution followed by the cessation of the function of assimilation, and (3) a great reduction in transpiratory power. It has been found that the activity of transpiration may be affected by excess of lime in the soil, by excess of water, by unfavourable climatic conditions, &c.

The appearance of chlorosis and the alteration in transpiration seem to be inseparable, and anything capable of modifying the one would necessarily influence the other. N. H. J. M.

Some Changes produced in Etiolated Plants. By GUSTAVE ANDRÉ (*Compt. rend.*, 1900, 130, 1198—1201).—The composition of

maize and lupin seeds is compared with that of normal and of etiolated plants about six weeks old. The carbon of the etiolated plants amounted to only about half the quantity present in the seeds, whilst there was a slight loss of total nitrogen. The maize seed contained 0.25 gram of asparagine in 100 seeds, and the etiolated plants 0.41 gram; in the case of lupins, the seeds contained 1.51 grams, and the etiolated plants 6.17 grams of asparagine. Amidic nitrogen (including nitrogen as asparagine) represents about half the total nitrogen in etiolated maize, and about nine-tenths the total nitrogen of lupins. These results, in conjunction with those relating to the carbohydrates soluble in water and the carbohydrates saccharifiable by dilute acids, indicate that the regeneration of proteids from asparagine and carbohydrates takes place more readily in maize than in lupins. In etiolated maize, there is a transformation of soluble carbohydrates into cellulose, whilst in the case of etiolated lupins the amount of cellulose remains stationary.

As regards ash constituents, it was found that silica was 30 times as abundant in etiolated maize as in the seed, and 15 times as abundant in the case of lupins. Etiolated maize contained 100 times as much lime as the seeds, but in etiolated lupins the amount of lime remained unchanged. The phosphoric acid both of etiolated maize and lupin plants remained about the same as in the seeds. Potash increased from 0.11 in maize seed to 0.72 in the etiolated plants and diminished from 0.46 in lupin seeds to 0.40 in the plants.

The relatively large amount of lime in etiolated maize plants is perhaps connected with the production of cellulose from soluble carbohydrates.

N. H. J. M.

Chemical Alteration of Rye and Wheat on becoming Mouldy. By R. SCHERPE (*Zeit. Unters. Nahr. Genussm.*, 1900, 3, 166).—With reference to the work of Dietrich, Hebebrand, and Welte, the author points out that grain, flour, and bread must not be regarded as identical media for the growth of micro-organisms.

M. J. S.

Manuring of Clover Hay. By J. R. CAMPBELL (*Rep. Tech. Instruct. Comm. Lancaster C.C.*, 1899, 11—13).—Sodium nitrate and ammonium sulphate applied alone gave almost the same results; but in conjunction with dung, or with a mixture of basic slag and potassium chloride, sodium nitrate gave a considerably greater increase than ammonium sulphate under the same conditions.

With sodium nitrate and basic slag, 1 cwt. of potassium chloride gave better results than half or twice the quantity.

Sodium nitrate, when applied with farmyard manure, produced an increase equal to that when applied alone.

N. H. J. M.

Manuring of Clover Hay. By J. R. CAMPBELL (*Rep. York. Coll. Leeds and E. and W. Ridings Joint Agric. Council*, No. 5, 1900, 8—12).—On chalk soil, potash manures had a decided effect in increasing the yield of red clover; the yellow trefoil was, consequently, largely suppressed. Basic slag alone did not increase the crop, but in conjunction with potassium chloride was decidedly beneficial; a

mixture of the two manures, 4 cwt. and 2 cwt. respectively, is recommended for clover-sick land.

Inoculation with nitragin had no appreciable effect.

N. H. J. M.

Experiments with Horse Beans on Soils of Various Origin under the same Climatic Conditions. By JOSEF SEISSL and EMANUEL GROSS (*Chem. Centr.*, 1900, i, 831; from *Zeit. landw. Versuchs-Wesen. Oesterr.*, 3, 153—162).—The results of pot experiments with six different soils: (1) clayey marl, (2) calcareous clay, (3) poor, red soil, (4) loose, humous loam, (5) sandy loam, rich in humus, and (6) loam poor in sand. No. 4 gave the best results, then 2, 5, 1, and 6 in the order given; No. 3 gave less than half the amount of produce obtained with No. 4.

As regards the plant constituents taken up from the soil, it was found that although the absolute amounts diminished, the relation in which they took part in production remained almost the same.

Analyses of the soil showed that in most cases a certain relation existed between the yield, the assimilation of phosphoric acid, and the proportions of phosphoric acid and sesquioxides on which the solubility of the phosphoric acid doubtless depends.

N. H. J. M.

Composition of the Very Rich Sugar-Beet of the Season 1898. By J. GRAFTIAU (*Ann. Science Agron.*, 1899, [ii], 5, ii, 173—178).—The analysis of a lot of twelve roots gave the following percentage results:

Water.	N.	Fat.	Sucrose.	N-free extract.	Cellulose.	Pure ash.
72.16	0.207	0.047	19.60	5.01	1.216	0.60

The ash contained K_2O , 31.7; CuO , 17.5; MgO , 9.83; and P_2O_5 , 10.17 per cent. The average weight of the roots was 400 grams, and they contained 93.21 per cent. of juice and 6.79 per cent. of marc. Comparing the results with those of previous years, it is seen that although the sugar was abnormally high in 1898 in the fresh roots, the results of this and other years do not differ much as regards sugar in dry matter. The nitrogen, the cellulose, and especially the pure ash, diminish as the sugar increases. As regards the ash constituents, the calcium increases slightly with the sugar, whilst the potassium and phosphoric acid greatly diminish in quantity as the percentage of sugar in the roots increase; and the magnesium remains fairly constant. This is in opposition to Corenwinder's theory that magnesium and phosphoric acid are absorbed in the form of ammonium magnesium phosphate.

N. H. J. M.

Experiments at Rothamsted on the Changes in the Composition of Mangels during Storage. By NORMAN H. J. MILLER (*Journ. Roy. Agric. Soc. Engl.*, 1900, [iii], 11, 57—64).—Samples of mangels from two plots of the permanent Root Crop Field were analysed as soon as possible after being taken up, and subsequently, at suitable intervals, until the end of June. Sugar, total nitrogen, and ash were determined at each date, and pentosans at the commencement

and in June. The results are calculated as percentages of the original weights of the roots (in October).

Series II, Plot I (manured with dung, basic slag, and potassium sulphate). Up to March 28, there was no decided change in composition, either as regards the amount or the nature of the sugar. But by June 20 there was a loss of about 1·4 per cent. of sugar, and about half the sugar had become inverted, whilst the loss of dry matter was about twice as great as that of the sugar; the pentosans diminished from 1·13 in October to 0·82 in June; whilst the total nitrogen at the two dates was nearly the same. There was a gain both of sugar and of nitrogen in the dry matter of the roots.

Series II, Plot II (same manures, with nitrate in addition). In these roots, loss of sugar (0·7 per cent.) had taken place early in January, and there was a further loss (0·66 per cent.) between January 6 and March 28; but from March to June the loss was less. The total loss of sugar in 8 months was 1·7 per cent., whilst the loss of total organic matter was 2·2 per cent. The inversion of the sugar began earlier, but was not so great as in Series II, Plot I. The percentage of pentosans was 0·97 in October, and 0·72 in June. The dry matter of the roots contained less sugar in June than in October, and rather more nitrogen.

In comparing the results obtained with the roots from the two plots, it is seen that the loss of sugar was greater and the loss of organic matter other than sugar much less under the influence of nitrate than without nitrate; in the one case, there was a tendency for the percentage of sugar in the dry matter to diminish and in the other to considerably increase.

As regards pentosans, the roots manured with nitrate contained rather less than the roots which received no nitrate (compare de Chalmont, *Ber.*, 1894, 27, 2722); and the loss was slightly less in the case of the nitrate plot.

Calculated in pounds per acre, it is seen that the loss of sugar was very considerable, especially in the case of the roots from Series II, Plot II. Owing, however, to the much greater yield of roots on this plot, the amount of sugar from the roots of an acre remained much in excess of the amount from Series II, Plot I. N. H. J. M.

Behaviour of Water-soluble Phosphoric Acid in Soils. By MARTIN ULLMANN and A. GRIMM (*Chem. Ind.*, 1900, 23, 61—69).—The results of numerous experiments with various soils showed that for months after the application of superphosphate, phosphoric acid soluble in water passed through a depth of soil equal to 25—27 cm. without being completely retained, either chemically or mechanically. It is not possible by determining the magnesia, lime, and sesquioxides in soil to estimate its absorptive power for phosphoric acid, as the results cannot show to what extent these substances are available. An artificial mixture of sand (300 grams) and freshly precipitated aluminium hydroxide (3 grams) completely absorbed 0·15 gram of soluble phosphoric acid at once, whilst with ferric hydroxide the absorption was complete in an hour. With soil (100 grams) containing 10·26 per cent. of ferric oxide and alumina, and 0·18 gram of

soluble phosphoric acid, 28.13 per cent. of the latter remained in solution after 66 hours, only a portion of the sesquioxides being available for fixing phosphoric acid.

In the case of soil containing 18.7 per cent. of lime as carbonate, in addition to 4.21 per cent. of ferric oxide and alumina, 20.24 per cent. of the soluble phosphoric acid remained dissolved after 66 hours, and 18.81 per cent. after 14 days.

The diffusion of water-soluble phosphoric acid in the soil depends on the amount and distribution of the rain. There is no evidence to show how far the fear of loss of soluble phosphoric acid in light, sandy soils is justified, but in the case of limed or marled sandy soil it has been shown that no loss takes place. The mechanical fixation of soluble phosphoric acid seems to depend on the amount of fine sand, and especially sand of the fineness of dust, in the soil.

Attention is called to the advantage of a supply of soluble phosphoric acid in the subsoil, and the conclusion is drawn that superphosphate is, in many cases, preferable to other phosphatic manures.

N. H. J. M.

Chemical Methods for ascertaining the Lime Requirement of Soils. By HENRY J. WHEELER, BURT L. HARTWELL, and C. L. SARGENT (*J. Amer. Chem. Soc.*, 1900, 22, 153—177).—The best method, of those tried, for ascertaining the lime requirement of upland acid soils in Rhode Island was found to be titration with ammonia. The soil (15 grams) is treated with about $N/10$ ammonia (100 c.c.) and distilled water (100 c.c.) and frequently agitated during about 42 hours. After being allowed to settle, a definite amount of the liquid is treated with hydrochloric acid (about $N/2$) at the rate of 5 c.c. to each 20 c.c. of solution, and made up to a definite volume. When the precipitated humus has settled, portions of 50 c.c. are titrated with ammonia, coralline being employed as indicator. The method is most suitable in the case of soils containing much humus. The gravimetric determination of humus in soils, without previous extraction with acid, also gave results more in accordance with the crop tests than the other methods.

Useful indications are obtained by observing the effect of the moistened soil on blue litmus paper, as compared with soil of known character; and (when the acidity is due to a great extent to organic matter) by treating the soil with dilute ammonia, and noting whether the liquid acquires a dark brown or black colour.

In the case of the upland acid soils, the methods of Hollemann (extracting the lime with water containing carbon dioxide, *Landw. Versuchs-Stat.*, 1892, 41, 38), and of Tacke (*Abstr.*, 1898, ii, 103), and extracting the lime with hot dilute hydrochloric acid, were found to be unsuitable. A new method, which it is thought may prove to be very useful when the most suitable conditions have been ascertained, is described, in which the soil is heated with calcium carbonate in presence of water and the carbon dioxide determined.

N. H. J. M.

Composition of the Soils of the Canton Redon as regards Lime, Magnesia, Potash, and Nitrogen. By G. LECHARTIER (*Compt. rend.*, 1900, 130, 1163—1166).—Analyses of soil samples re-

presenting the soils of different geological origin in the Canton of Redon, in the Department Ille-et-Vilaine, are given. The formations from which the various soils are derived are granite, pre-Cambrian, Silurian, Upper Silurian, and ancient and modern alluvium. The average amounts of lime and magnesia are 0.58—1.08 and 0.84—1.60 per thousand. In some cases, soils which produce 20—30 hectolitres of wheat per hectare contain only 0.26—0.28 per thousand of lime on the pre-Cambrian, and 0.67—0.80 per thousand on the Angers schists. The soils are rich in potash, and only on 6—7 per cent. of the whole area is the amount of potash in the soil less than 0.2 per cent.; the average amounts are 0.232—0.577 per cent.

The soils contain on the average 0.109—0.135 per cent. of nitrogen, and 2.37—4.18 per cent. of organic matter, determined by Raulin's method. N. H. J. M.

Arable Soils of the Canton of Redon with respect to Phosphoric Acid. By G. LECHARTIER (*Compt. rend.*, 1900, 130, 1225—1229. Compare preceding abstract).—The cultivated soil of half the area of the Canton contains more than 0.1 per cent. of phosphoric acid. The average amounts of phosphoric acid in the soils derived from the different geological formations are as follows: granite, 0.87; pre-Cambrian, 0.90; Armorican sandstone, 0.57; Angers schist, 1.04; Poligne schist and sandstone, 1.05; and alluvium, 1.24 per cent.

Phosphatic manuring was found to be beneficial even in the case of soils containing more than 0.1 per cent. of phosphoric acid. Both the yield and the quality of wheat, grown in rotation, was benefited by phosphates; and fossil phosphates and basic slag had more effect than superphosphate. N. H. J. M.

Analysis of Siberian Arable Soil. By A. SEMPOLOWSKI (*Chem. Centr.*, 1900, i, 831; from *Zeit. landw. Versuchs-Wesen Oester.*, 3, 163—164).—The sample of soil was obtained from the steppe near Omsk, where the land had been ploughed once. The soil contained: Stones, 0.014; coarse gravel, 0.046; fine gravel, 1.050; coarse sand, 1.362; fine sand, 13.630; sand as dust, 55.115; and clay, 28.773 per cent. The chemical composition of the dry soil was as follows: Humus, 11.57; N, 0.57; K_2O , 0.16; CaO , 0.93; and P_2O_5 , 1.00 per cent. The absorptive power for water is 35.84 per cent.

Experiments with sugar beet gave unsatisfactory results; the roots were small, and the juice had a very low purity coefficient.

N. H. J. M.

Use of Nitragin and Alinit for the Growth of Beans and Oats respectively. By J. R. CAMPBELL (*Rep. Tech. Instruction Comm. Lancaster C.C.*, 1899, 36—37).—Experiments with beans and clover made in 1897 seemed to indicate that inoculation with nitragin was beneficial. In 1898, negative results were obtained.

Alinit had no apparent effect.

N. H. J. M.

Experiments with Alinit. By HJALMAR VON FEILITZEN (*Mitt. Ver. Förd. Moorkultur*, 1900, 18, 41—44).—Black Tartarian oats were

grown in peaty soil in zinc vessels having an area of 0.283 sq. m. All the vessels received slaked lime (6000 kilos.), basic slag (800 kilos.), and potash manure (96 kilos. per hectare); one set had no further manure, another had alinit, and a third set nitrogen as ammonium sulphate and sodium nitrate. The following yields were obtained (grams):

Kainit.			38 per cent. potash manure.		
Without N.	Alinit.	With N.	Without N.	Alinit.	With N.
167.5	156.0	434.0	133.5	123.5	369.0

Field experiments on peat land furnished similar results; both the yield of grain and of straw were much less under the influence of alinit than without alinit, whilst sodium nitrate very greatly increased the yield.

In field experiments on poor, sandy soil, the effect of inoculation with alinit was compared with that of different amounts of sodium nitrate. The smallest amount of nitrate (100 kilos.) produced considerably more grain and straw than was obtained on the alinit plot.

N. H. J. M.

Alinit. By BRUNO TACKE (*Mitt. Ver. Förd. Moorkultur* (1900, 18, 37—41).—Oats, barley, and summer rye were grown in peaty soil in pots, without nitrogenous manure, with sodium nitrate and with alinit respectively. Mineral manures were applied to all the pots. Similar experiments were also made on plots.

In the case of the pot experiment, the application of alinit resulted, on the whole, in a slightly diminished yield, owing possibly to denitrification. In the field experiments with rye, barley, and oats, the yield was considerably less under the influence of alinit than on the plots which were not inoculated, whilst nitrate, in every case, increased the yield. In the case of black oats, the yield of the alinit plot was greater than that of the plot which had no alinit, but much less than that of the nitrate plot. It is, however, not thought that the alinit had any beneficial effect.

N. H. J. M.

Analytical Chemistry.

Apparatus for Measuring Evolved Gases at Constant Volume. By ANDRÉ JOB (*Bull. Soc. Chim.*, 1900, [iii], 23, 288—291). —This apparatus is of use in the analysis of carbonates, carbides, sulphides, carbamide, &c., the gases evolved by the decomposition of these substances in a closed vessel being estimated by the increase in pressure observed. It consists of a bulb or flask, connected with a delicate mercurial manometer, into the neck of which fits a graduated pipette furnished with a stopper so arranged that the liquid run into the flask is replaced by the air in the apparatus itself. Before each experiment, the apparatus is brought to a known temperature by im-

mersion in water, and the pressure made equal to that of the atmosphere; the acid or other liquid in the pipette is then allowed to flow into the flask, which may be heated if necessary, and the apparatus finally brought to the original temperature and the manometer read. If h is the increase in pressure, V the capacity of the apparatus, and t the temperature, the volume of the gas evolved is $Vh/760(1 + at)$.

N. L.

Hydro-Gasometer and Urinometer. By E. BENOIT (*J. Pharm.*, 1900, [vi], 11, 454—458).—The apparatus consists of a bottle (A) closed with a cork through which a tube passes. This tube is connected to another tube which passes through a cork inserted in one neck of a three-necked Woulff's bottle. Through the cork in the second neck of the Woulff's bottle, a thistle funnel is inserted, to act as a safety tube, and through the cork in the third neck a tube bent twice at right angles is inserted; one end of this tube dips under the water contained in the Woulff's bottle. The gas evolved in the bottle (A) forces the water out of the Woulff's bottle, and by collecting this water in a graduated cylinder, the volume of the gas evolved is ascertained.

H. R. LE S.

New Electrodes for Electrolytic Estimations. By AUGUSTE HOLLARD (*Bull. Soc. Chim.*, 1900, [iii], 23, 291—292).—The electrode on which the element is to be deposited consists of a nearly cylindrical, truncated cone of platinum foil, whilst the other electrode consists of a spiral of platinum wire inside, and a wire cage outside, the cone. The advantages claimed are rapid and regular deposition, and an equable evolution of gas, whereby loss through spirting is avoided.

N. L.

A New Indicator. By JULIUS FORMÁNEK (*Zeit. anal. Chem.*, 1900, 39, 99—103).—Alizarin-green-B (Dahl and Co.) dissolves in water with a dirty green colour; in alcohol, more sparingly, with a flesh colour. Acids added to either of these solutions produce a carmine red colour, alkalis a pure green. It is affected by carbon dioxide as by an acid. In presence of ammonium salts, its indications are uncertain. Aluminium salts behave like free acids, even in presence of precipitated aluminium hydroxide. This indicator can be used by artificial light. M. J. S.

New Indicator for Acidimetry; Estimation of Boric Acid. By JULES WOLFF (*Compt. rend.*, 1900, 130, 1128—1131).—Ferric salicylate dissolved in a solution of sodium salicylate develops a violet coloration in dilute mineral acids, which changes to orange when the solutions are neutralised or rendered alkaline by sodium hydroxide; the acid reaction is, however, not produced by boric, phosphoric, or hydrofluoric acid, and the end point is not affected by the presence of ammonium sulphate. Similar reagents may be obtained from other aromatic ortho-hydroxy-acids.

In estimating the boric acid present in a borate, the solution of the salt is acidified with sulphuric acid, and the excess of mineral acid removed by means of standard alkali, the end point being determined by the above indicator. Glycerol and phenolphthalein are now

added to the solution, and the titration of the boric acid is effected in the usual manner (compare this vol., ii, 312). G. T. M.

Iceland Spar as a Standard in Volumetric Analysis. By ORME MASSON (*Chem. News*, 1900, 81, 73—75).—Iceland spar in lumps of a gram to three grams in weight, freed from dust and sharp edges by treating with dilute hydrochloric acid, and then washing and drying, is used in quantities of about 3 grams; it is weighed in the beaker, which is covered with a glass. Twenty c.c. of the acid to be tested are run in, and when action has ceased, the sides and cover of the beaker are washed down, and the whole heated to and kept at boiling temperature for an hour. The calcium chloride solution is decanted off, the beaker and residual spar well washed, dried, and weighed. The strength of the acid is calculated from the loss in weight.

D. A. L.

Separation and Identification of Acids. By RICHARD ABEGG and W. HERZ (*Zeit. anorg. Chem.*, 1900, 23, 236—239).—The authors give a systematic method for the qualitative examination of the acids of a mixture, analogous to those in general use for the bases. The substance is (i) boiled with dilute hydrochloric or nitric acid, whereby carbon dioxide, sulphur dioxide, nitrogen trioxide, hydrogen cyanide, hydrogen sulphide, and acetic acid are evolved, and are identified by special tests. (ii) The substance is boiled with concentrated sodium carbonate solution, the filtrate treated with hydrochloric acid, made alkaline with ammonia, and treated with calcium chloride. A precipitate insoluble in acetic acid indicates the presence of a fluoride or oxalate; a precipitate soluble in acetic acid indicates the presence of a cyanide, succinate, arsenite, arsenate, or phosphate. (iii) The filtrate from (ii) is treated with barium chloride. A precipitate soluble in hydrochloric acid indicates the presence of a chromate or dichromate; a precipitate insoluble in hydrochloric acid indicates the presence of a sulphate or silicofluoride. (iv) The filtrate from (iii) is neutralised with hydrochloric acid and zinc chloride added. A brownish-yellow precipitate indicates the presence of a ferricyanide, and a white precipitate the presence of a ferrocyanide. (v) A small quantity of the filtrate from (iv) is treated with a small quantity of a ferric salt. A permanent red coloration indicates the presence of a thiocyanate, and a red coloration disappearing on boiling with the formation of a precipitate the presence of an acetate. (vi) In the absence of a thiocyanate, the filtrate from (iv) is treated with a solution of silver nitrate (nitric acid and nitrates being used in place of hydrochloric acid and chlorides in all previous operations). A precipitate indicates the presence of a chloride, bromide, or iodide. (vii) An aqueous solution of the original substance is tested for a nitrate by means of a ferrous salt. Oxyhalogen acids are indicated by the evolution of oxygen on igniting the original substance. E. C. R.

Volumetric Estimation of Bromides in Presence of Iodides and Chlorides. By JULIUS VON WESZELSZKY (*Zeit. anal. Chem.*, 1900, 39, 81—91).—In moderately acidified solutions, hydriodic acid is converted into iodic acid by chlorine, whilst from hydrobromic acid

the bromine separates in the free state. In alkaline solutions, bromides are oxidised to bromates. A mixture, containing the three halogen salts, is therefore acidified, treated with chlorine water, and distilled in a stream of carbon dioxide into a solution of potassium hydroxide. The retort with a bulbed neck, employed by Bunsen and Fresenius for the absorption of chlorine, forms a suitable receiver; the still should consist entirely of glass. When the carbon dioxide is no longer absorbed, the contents of the receiver are boiled to dryness to expel chlorine and hypochlorous acid, and convert hypochlorite entirely into chlorate. The residue is dissolved, mixed with some potassium iodide and acidified, and the liberated iodine titrated with thiosulphate. The iodate in the still can also be estimated by adding potassium iodide and titrating the iodine. In the absence of iodides, potassium carbonate and chlorine are added to the original solution, which is then boiled down and treated as before. Arsenic and antimony must first be removed by hydrogen sulphide, and iron, by boiling with the alkaline carbonate and filtering before adding chlorine. M. J. S.

Estimation of Ozone. By NICOLAE TECLU (*Zeit. anal. Chem.*, 1900, **39**, 103—105).—The gas in which ozone is to be estimated is enclosed in a glass tube of pipette form between two stopcocks. A solution of potassium iodide is forced into the tube by mercury pressure, and shaken with the gas for 5 minutes. It is then acidified with acetic acid to decompose any iodate which has been formed, and is titrated with thiosulphate. Any blue colour which is developed after its first disappearance is to be neglected. 1 c.c. of *N*/100 thiosulphate = 0.00008 gram of ozone. M. J. S.

Detection of Sulphates in Presence of Thiosulphates. By LEONARD DOBBIN (*Pharm. J.*, 1900, [iv], **10**, 182).—Barium sulphate is perceptibly soluble in solution of sodium thiosulphate, especially in the presence of a little free nitric acid.

Salzer has recommended converting the thiosulphate into tetrathionate by means of iodine before testing for sulphate, but the author thinks that the detection of sulphate is best accomplished by using the method devised by Grossman. The liquid is heated in a current of carbon dioxide, hydrochloric acid is added, and the sulphur dioxide expelled by prolonged boiling. The remaining liquid is filtered and tested for sulphate with barium chloride. L. DE K.

Estimation of Nitric Nitrogen by Schlösing's Method. By C. DAVIDSON (*Chem. News*, 1900, **81**, 97—98).—A modification of de Koninck's apparatus (*Abstr.*, 1894, ii, 296) is described; in it a descending tube, 800 mm. long and 2 mm. bore, is used to connect the distilling flask to the lower side tube of a modified Schiff's nitrometer, the lower part of which is charged with mercury nearly to the level of the other side tube, which is connected with an air-free water supply. The gas burette is furnished with a T-piece at the top, to the middle limb of which the top of the modified Schiff nitrometer is attached by means of a capillary tube, the other limb carrying a funnel with a clip at the connection. In use, air is driven out from the intermediate vessel and at this funnel by the air-free water; the

gas burette is charged from its reservoir with soda right into the funnel, and subsequently the intermediate vessel and the gas burette are put into connection for the transference of the nitric oxide produced.

D. A. L.

Detection of Nitrous Acid in Water by Means of Amino-naphthol-K-Acid [1-Amino-8-hydroxynaphthalene-4:6-disulphonic Acid]. By H. MENNICKE (*Zeit. angew. Chem.*, 1900, 235—236).—The author strongly recommends Erdmann's process (this vol., ii, 243) as affording the most delicate test as yet known for the detection of nitrites in drinking water. Nitrates do not interfere. It is possible to detect the presence of 1 part of sodium nitrite in 300,000,000 parts of water. The test is best made in daylight.

L. DE K.

Detection of Nitric Acid in Water and in Milk. By F. UTZ (*Chem. Centr.*, 1900, i, 875; from *Pharm. Zeit.*, 45, 229—230).—Cimmino's modified diphenylamine test is recommended if conducted in the following manner. The water or the milk serum is mixed with a little of the diphenylamine reagent, put into a test-tube, and strong sulphuric acid is carefully poured down the side. At the place of contact a more or less intense blue ring is formed. When milk is kept for a long time, the lactic acid bacteria destroy any nitrates.

L. DE K.

Hygienic Significance of Nitrites in Drinking Water. By EDUARD SCHÄER (*Ber.*, 1900, 33, 1232—1236).—A theoretical paper, in which the author discusses the origin of nitrites in drinking water, and endorses Spiegel's conclusion (this vol., ii, 318) as to their being of little value for hygienic diagnosis; no new facts are adduced.

W. A. D.

Connection Between the Chlorides and Nitrates in the Polluted Well Waters in Inhabited Localities. By JOSEF KÖNIG (*Zeit. Unters. Nahr.-Genussm.*, 1900, 3, 228—233).—Attention is directed to the already well-known fact that in well waters which have been contaminated with sewage there is generally an intimate relation between the chlorides, nitrates, and sulphates present. Waters which are unquestionably free from animal pollution may contain large amounts of one or other of these impurities, and even be very rich in bacterial life, but the simultaneous presence of large proportions of all of them, if the conditions as to locality are such that contamination is possible, point unmistakably to its occurrence.

M. J. S.

Estimation of Arsenic in Metals and Alloys. By AUGUSTE HOLLARD and L. BERTIAUX (*Bull. Soc. Chim.*, 1900, [iii], 23, 300—302).—The arsenic is separated by distillation with hydrochloric acid and ferric sulphate, and titrated with iodine solution in the usual manner. Antimony is retained by passing the vapours through a U-tube filled with glass beads and heated in an oil-bath at 150—175°. The process is inexact when applied to the estimation of arsenic in antimony, since about 0.03 per cent. of the latter passes over into the distillate.

N. L.

Detection of Boric Acid in Borates. By HUGO BORNTRÄGER (*Zeit. anal. Chem.*, 1900, 39, 92).—When heated on platinum foil, boric acid colours a Bunsen flame green; borates do not. Borates when similarly heated with hydrofluoric acid or with ammonium nitrate and chloride, or with mixtures of sulphuric and hydrochloric acids, sulphuric and nitric acids, or hydrochloric and nitric acids (but not with one of the acids alone) give an instantaneous and intense green coloration. The reaction is more sensitive than that with sulphuric acid and alcohol. M. J. S.

Absorption Apparatus for Elementary Organic Analysis. By FRANCIS G. BENEDICT (*Amer. Chem. J.*, 1900, 23, 323—334).—The water formed during a combustion is absorbed by bubbling through concentrated sulphuric acid contained in the bend of a 5" U-tube, the second limb containing glass-wool moistened with the same acid to finally dry the gas; any condensed water is allowed to drop into a small vial supported in the first limb above the acid on a piece of glass rod flattened at one end. The carbon dioxide is absorbed in a U-tube by specially prepared moist soda-lime, whilst another U-tube acting as a guard tube, is one-third filled with soda lime and two-thirds with pumice moistened with concentrated sulphuric acid, a plug of glass wool separating the two. The advantage of this apparatus over that ordinarily employed is discussed; a description is appended of a modified calcium chloride jar, which serves to free the air or oxygen used in a combustion from both water and carbon dioxide in a single vessel. W. A. D.

Estimation of Carbon and Hydrogen by Combustion in Oxygen using Copper Oxide. By CHARLES F. MABERY and WILLIAM R. CLYMER (*J. Amer. Chem. Soc.*, 1900, 22, 213—218).—From the authors' experiments, it appears that the best results in the analysis of hydrocarbons are obtained when the combustion tube containing the copper oxide has been used a few times.

The water formed during the combustion is best absorbed in a U-tube containing 3 c.c. of strong sulphuric acid, a bulb being attached to condense the greater part of the water; the quantity of carbon dioxide retained by the acid is very trifling. The carbon dioxide is best absorbed in a Geissler apparatus containing aqueous potassium hydroxide of 33.3 per cent. strength, the usual calcium chloride tube being attached; no advantage is gained by using phosphoric oxide instead of fused calcium chloride.

The air and oxygen used in the experiment should be purified by passing through two long bent tubes containing broken glass moistened with 40 per cent. aqueous potassium hydroxide and strong sulphuric acid respectively. L. DE K.

Elementary Analysis of Organic Substances containing Nitrogen. By FRANCIS G. BENEDICT (*Amer. Chem. J.*, 1900, 23, 334—352).—When a substance containing nitrogen not directly combined with oxygen is first charred in the closed combustion tube (that is, without a current of air or oxygen), and the non-volatile residue subsequently oxidised by the admission of oxygen, no oxides of

nitrogen are produced; in the case, however, of nitro-compounds, and especially of nitrates of organic bases, the results are vitiated by the formation of these oxides. Instead of employing a copper spiral in the fore-part of the tube to reduce the oxides, the author mixes with the substance analysed a known weight of either pure cane sugar (in the form of powdered sugar-candy) benzoic acid, or naphthalene; the finely-divided copper produced in the reduction of the copper oxide by this excess of oxidisable material is sufficient to completely reduce any oxides of nitrogen formed. This method obviates the error usually introduced in a combustion owing to the presence of either hydrogen, water, or carbon dioxide in the copper spiral employed. In the case of explosive compounds, the combustion is rendered more regular by mixing the substance with 3 or 4 times its bulk of finely powdered, pure quartz. In the case of highly nitrated substances, it is noteworthy that this admixture has a direct influence on the reduction of nitrogen oxides; although not completely reduced, these are now present in much smaller quantities, so that without the addition of a reducing material such as cane sugar or benzoic acid, the results obtained for carbon are sufficiently accurate for most purposes, although the percentage of hydrogen is somewhat too high.

A large number of analyses are given showing the universal application of the method described, and the degree of accuracy of the results obtained.

W. A. D.

Repeated Use of Copper Potassium Chloride for the Solution of Steel or Iron in estimating Carbon. By GEORGE W. SARGENT (*J. Amer. Chem. Soc.*, 1900, **22**, 210—213).—The solution of copper potassium chloride, when used in the estimation of carbon in steel or iron, gradually becomes converted into the cuprous state, but may be rendered again fit for use by passing a current of chlorine. In this way, it may be used over and over again until it becomes too saturated with iron.

L. DE K.

Direct Combustion of Metallic Alloys. By HARRY BREARLEY (*Chem. News*, 1900, **81**, 91—92).—With regard to the direct estimation of carbon in alloys, &c., in the case of tungsten, ferro-tungsten (85 and 50 per cent.), ferro-silicon, 12 per cent. silicon-spiegel, ferro-silico-molybdenum, molybdenum, and 70 per cent. molybdenum-nickel, satisfactory decarbonisation has been achieved by 1 hour's combustion of the material passed through a 90-mesh sieve, in a current of oxygen at a high temperature, a porcelain tube supported on asbestos arches being employed. With 20 per cent. spiegel, 70 per cent. tungsten-nickel, 80 per cent. ferro-manganese, 60 per cent. ferrochromium, 70 per cent. chromium-nickel, and chromium, however, decarbonisation was imperfect under the same circumstances.

D. A. L.

Substitutes for Hydrochloric Acid in Testing Carbonates. By JOSEPH W. RICHARDS and NORMAN S. POWELL (*J. Amer. Chem. Soc.*, 1900, **22**, 117—121).—For use in the field, the authors prefer using solid acids for the identification of native carbonates as being more easy to carry in a portable set of apparatus. Before use, they are dissolved in boiling water.

A 20 per cent. solution of tartaric acid is the best, citric acid coming next. A 10 per cent. solution of oxalic acid does not give such a plain effervescence as the others. A 20 per cent. solution of potassium hydrogen sulphate also gives a satisfactory result except in the case of witherite and phosgenite; it must be remembered that sulphides also give effervescence.

L. DE K.

Technical Estimation of Zinc. By ALBERT H. LOW (*J. Amer. Chem. Soc.*, 1900, 22, 198—202).—The author's process is devised for zinc ores from Colorado, but with suitable modifications it may no doubt be applied also to other zinc ores.

A solution of potassium ferrocyanide containing 22 grams of the crystallised salt per litre is standardised by dissolving 0.1 gram of pure zinc in 6 c.c. of strong hydrochloric acid, and adding 10 grams of ammonium chloride and 200 c.c. of boiling water. The ferrocyanide is then added until a drop of the liquid strikes a brownish colour with solution of uranium nitrate.

0.5 gram of the ore is boiled in a pear-shaped flask with 5 c.c. of nitric acid and 2 grams of potassium nitrate, 10 c.c. of a saturated solution of potassium chlorate in nitric acid are added, and the whole evaporated to complete dryness. When nearly cold, 30 c.c. of a solution containing 200 grams of ammonium chloride, 350 c.c. of water, and 500 c.c. of ammonia are added, and the contents boiled for 2 minutes; the solution is filtered and the undissolved matter washed with a hot solution of ammonium chloride containing 100 grams of the salt and 50 c.c. of ammonia to the litre. The filtrate is neutralised with hydrochloric acid, and 6 c.c. of the latter are then added in excess. After diluting to about 150 c.c., any copper, cadmium, and the bulk of the lead are precipitated by adding 50 c.c. of a saturated solution of hydrogen sulphide. After filtering, which is, however, only necessary if there is an abundant precipitate, the liquid is heated, and about one-third is poured into a beaker and set aside. The remainder is then titrated as described, and the greater part of the reserve liquid being added, the titration is continued; finally, the remainder of the reserve liquid is added and the titration cautiously finished. Both in this titration and in the "check," the true end-point is always slightly passed, as it always requires one or more drops of the ferrocyanide solution to get the uranium reaction, but this may be ascertained by a direct experiment.

Attention is called to the great importance of carefully following the directions as to the amount of free acid. Arsenic, when present in large amount, sometimes gives trouble by retaining iron in the ammoniacal solution. In this case, the ore should be subjected to a preliminary treatment. 0.5 gram of the sample is treated with 10 c.c. of strong hydrochloric acid and 1 c.c. of bromine, gently warmed for a few minutes, and finally boiled to dryness; the arsenic will thus be sufficiently expelled. Potassium nitrate and nitric acid are added, and the analysis proceeded with in the usual manner.

With some ores, it may be necessary to resort to a fusion before dissolving in acid.

L. DE K.

Volumetric Estimation of Red Lead. By JAMES F. TOCHER (*Pharm. J.*, 1900, 10, 310—312).—*1st Method.*—2.064 grams of the sample are heated with 50 c.c. of nitric acid of sp. gr. 1.2; 50 c.c. of $N/5$ solution of oxalic acid are added, and when the lead peroxide has disappeared, the liquid is partly neutralised with barium hydroxide. Solution of sodium sulphate is now added to precipitate the lead and barium, and after adding some dilute sulphuric acid to decompose any barium oxalate, the excess of oxalic acid is titrated with $N/5$ permanganate. One c.c. of oxalic acid decomposed by the lead peroxide represents 3.3 per cent. of red lead.

The matter may be simplified by treating the sample with 50 c.c. of nitric acid of sp. gr. 1.3 and adding the oxalic acid from a burette until the last trace of lead peroxide has disappeared.

2nd Method.—3.415 grams of the sample are heated with hydrochloric acid, the chlorine evolved is passed through a solution of potassium iodide, and the liberated iodine is titrated with $N/10$ sodium thiosulphate; each c.c. represents 1 per cent. of red lead.

3rd Method.—1.032 gram of the sample is heated with 20 c.c. of $N/5$ nitric acid and 20 c.c. of neutral hydrogen peroxide in a retort, the drawn-out neck of which dips into N soda, which should not be in excess. When the lead peroxide is decomposed, the flame is removed, and the soda solution allowed to enter the retort. Excess of sodium sulphate is added, then phenolphthalein, and the free nitric acid titrated with normal soda. Ten times 100 (representing 20 c.c. of $N/5$ nitric acid) — number of c.c. of soda required for neutralisation, gives the percentage of total lead in the sample. If only the lead peroxide is to be estimated, the sample is first treated with dilute nitric acid, and the undissolved matter is collected on a filter; or the decomposed mixture is carefully poured on to a saturated solution of sodium and potassium nitrates, contained in a conical vessel, when the lead peroxide sinks to the bottom, and the acid liquid may be siphoned off; the deposit is then treated with hydrogen peroxide as directed.

L. DE K.

Estimation of Thallium. By VICTOR THOMAS (*Compt. rend.*, 1900, 130, 1316—1319).—Soluble thallos salts are oxidised to the thallic condition by auric bromide (bromoauric acid, HAuBr_4), an equivalent amount of gold being precipitated; the latter is collected and weighed. The amount of thallium present is obtained by multiplying the weight of this precipitate by the factor 1.5533. The quantity of thallos compound taken for analysis should correspond with 0.2—0.3 gram of the pure chloride.

The auric bromide is conveniently prepared by dissolving gold in a mixture of bromine and hydrobromic acid, and evaporating the solution to the crystallising point.

G. T. M.

Analysis of Commercial Copper. By AUGUSTE HOLLARD (*Bull. Soc. Chim.*, 1900, [iii], 23, 292—300).—A detailed scheme for the complete analysis of commercial copper is given. The metal is dissolved in a mixture of sulphuric and nitric acids, and the copper, together with silver, deposited electrolytically, using the author's

form of electrodes (this vol., ii, 435). Since arsenic and antimony are usually present in sufficient quantity to be deposited along with the last traces of copper, it is advisable to stop the electrolysis before the whole of the copper is deposited, and to estimate the remainder after removing arsenic and antimony. The arsenic is precipitated by hydrogen sulphide in concentrated hydrochloric acid solution, and the filtered liquid diluted with an aqueous solution of hydrogen sulphide, whereby the sulphides of copper and antimony are precipitated. The mixed sulphides are dissolved in potassium cyanide solution, and the antimony estimated electrolytically, whilst the residual copper is estimated colorimetrically or electrolytically after removal of the cyanide. In the liquid from which copper, arsenic, and antimony have been removed, the iron is precipitated by ammonia, and the precipitate dissolved in hydrochloric acid and titrated with iodine solution. The nickel and cobalt still remaining in solution are deposited electrolytically in presence of ammonium sulphate, according to Fresenius and Bergmann's process. For the estimation of lead a fresh quantity of the metal is dissolved in nitric acid, and the solution electrolysed, the lead being deposited as peroxide on the anode. The electrolytically deposited copper, or a fresh portion of the original metal, is dissolved in nitric acid, and the silver precipitated by hydrochloric acid; the precipitate is dissolved in potassium cyanide solution and the liquid electrolysed, the metal being either weighed as such, or dissolved in nitric acid and titrated with potassium thiocyanate solution. Arsenic is estimated by the Hollard and Bertiaux's process (this vol., ii, 438). Gold is determined by treating a large quantity of the metal with nitric acid and cupelling the insoluble residue. Sulphur is estimated as barium sulphate in the nitrohydrochloric acid solution of the metal. N. L.

Volumetric Estimation of Corrosive Sublimate in Dressing Materials. By MARTIN LEHMANN (*Chem. Centr.*, 1900, i, 876; from *Pharm Zeit.*, 45, 209—210).—Twenty grams of the material are treated in a 500 c.c. stoppered flask with 200 c.c. of a 0.5 per cent. solution of sodium chloride at 70—80°, and left for 24 hours at 25—30°, with frequent shaking; 100 c.c. of the solution are then carefully evaporated to 10—15 c.c. A loss of mercuric chloride is not to be feared, as its double sodium salt is not volatilised with water vapour. The solution is now slowly poured into 20 c.c. of *N*/100 alkali, the mixture is gently warmed, and the excess of alkali titrated with *N*/100 hydrochloric acid, using phenolphthalein as indicator. L. DE K.

Estimation of Manganese as Pyrophosphate. By WILHELM BÖTTGER (*Ber.*, 1900, 33, 1019—1022).—Accurate results can be attained in the estimation of manganese as pyrophosphate by precipitating with ordinary sodium phosphate in a neutral solution to which 5—10 mol. of an ammonium salt have been added. The precipitate must be washed with cold water containing a little ammonia until no residue is left on evaporating the filtrate and igniting. A. H.

Estimation of Manganese as Sulphide. By JOHN PATTINSON and HUGH S. PATTINSON (*Chem. News*, 1900, 81, 193).—When the sul-

phide method of estimating manganese is employed, the sulphide precipitate should be examined for barium, cobalt, iron, silicon, calcium, magnesium, &c., and the filtrate should be acidified, treated with bromine to oxidise separated sulphur, then mixed with excess of ammonia and bromine, and any precipitate of manganese added to the main sulphide precipitate. D. A. L.

Electrolytic Estimation of Manganese in Manganese Ores. By ARTHUR HIORNS (*Chem. News*, 1900, 81, 15).—The solution, which should not contain more than 0.03 gram of manganese, should be made strongly acid with nitric acid, and be kept so during the operation. A tared platinum dish serves for the positive electrode, a spiral of platinum wire for the negative, and when the current is started the temperature is raised to, and maintained at, 60°. Twelve hours suffices for the deposition of all the manganese, which is washed, dried, ignited, and weighed as Mn_3O_4 . D. A. L.

Estimation of Manganese in Steel. By HORACE JERVIS (*Chem. News*, 1900, 81, 171—172).—In the method of estimating manganese by dissolving the sample in nitrosulphuric acid, oxidising with red lead, and titrating the filtrate with ferrous sulphate and permanganate, the quantity of the latter reagent consumed at first increases with the amount of manganese present, but when a maximum of 0.180 per cent. of manganese in the solution in the presence of iron, or 0.224 per cent. in the absence of iron, is attained, any further increase in the manganese causes a corresponding decrease in the consumption of permanganate. D. A. L.

Soluble Ferric Pyrophosphate. By W. E. RIDENOUR (*Chem. Centr.*, 1900, i, 834; from *Amer. J. Pharm.*, 72, 125—128).—The author has modified the orthophosphate test of the U.S. Pharmacopœia for the purity of soluble iron pyrophosphate as follows: 1 gram of the sample is boiled with 10 c.c. of aqueous potassium or sodium hydroxide to remove the iron, the filtrate is acidified with hydrochloric acid, ammonia is added in slight excess, and then magnesium mixture (10 grams of magnesium sulphate, 20 grams of ammonium chloride, dissolved to 120 c.c.) as long as a precipitate is formed; this precipitate should be soluble in a slight excess of acetic acid, and should not reappear on boiling the solution.

If the sodium pyrophosphate used in the preparation of the iron compound is free from orthophosphate, there is no fear of the latter containing any orthophosphate, no transformation occurring. L. DE K.

Analysis of Molybdenum Alloys. By HUGO BORNTÄGER (*Zeit. anal. Chem.*, 1900, 39, 91).—About a gram of the alloy is dissolved in 50 c.c. of aqua regia, the solution evaporated to dryness, and the nitric acid expelled by hydrochloric acid. The residue is treated with 50 per cent. alcohol, when most of the molybdenum will remain undissolved as molybdic acid, but part dissolves as chloride. The solution is evaporated to dryness, and the residue again treated with 50 per cent. alcohol, when the remainder of the molybdenum is obtained as molybdic acid (compare Abstr., 1898, ii, 649). M. J. S.

Separation of Tungsten and Molybdenum. By FRED IBBOTSON and HARRY BREARLEY (*Chem. News*, 1900, 81, 13—15).—Heating mixtures of molybdic and tungstic oxide in a muffle is not adapted to the direct estimation of the molybdenum. In such mixtures, 90 per cent. of the molybdenum volatilises readily, but the remaining 10 per cent. requires prolonged and strong heating for its expulsion. The separation of these oxides by means of hydrochloric acid is imperfect, the molybdic anhydride not being absolutely soluble and the tungstic anhydride not absolutely insoluble. A procedure recommended is to precipitate the two together by means of lead acetate, wash slightly with hot, very dilute acetic acid, ignite, dissolve the residue by heating gently with concentrated hydrochloric acid, using 1 c.c. for each centigram of lead salt, then add two or three times the volume of boiling water, boil, redissolve the precipitate in hydrochloric acid, reprecipitate with water, and determine the molybdenum as lead molybdate. When the proportion of tungsten is small, the solution of the ignited lead salts is evaporated to a pasty consistency with a few drops of nitric acid, treated with 100 to 200 c.c. of dilute hydrochloric acid (3 : 1), and boiled.

D. A. L.

Test for Tin. By ALLEN ROGERS (*J. Amer. Chem. Soc.*, 1900, 22, 220—221).—The usual ammonium molybdate solution is stated to be a very delicate confirmatory test for stannous chloride, with which it produces a dark blue colour, even if the amount of stannous chloride does not exceed 0.000021 gram per c.c. Even when this solution is diluted five times, and consequently does not give any reaction with mercuric chloride, it still shows a faint blue tint with the molybdic reagent.

L. DE K.

Detection of small Quantities of Gold in Ores. By THEODOR DÖRING (*Chem. Centr.*, 1900, i, 734—735; from *Berg.-Hüttenm. Zeit.*, 59, 73—76, 97—99. Compare this vol., ii, 371).—The ore is treated with a volatile iodine compound, such as ammonium iodide containing free iodine, or preferably with a solution of bromine in ether. Into the solution is dipped, six times in succession, a strip of filter paper 10 cm. long and 2 c.c. wide; this is then burnt, when, if gold is present, it will leave an ash of a purple colour, or if the solution contained more than 0.007 per cent. of gold, the colour will be yellow or brownish-red. The reaction is interfered with by the presence of iron or platinum should these metals have passed into the solution. The filter paper is prepared by soaking ash-free filter paper into a solution of magnesium nitrate containing 0.1 per cent. of magnesium oxide, and then exposing it, when dry, to the fumes of ammonium carbonate. An alternative process is given, based on the formation of purple of Cassius, which is a modification of Ohly's method. 100 grams of the finely-powdered and roasted ore are treated in a glass-stoppered bottle with 2 c.c. of a mixture of equal volumes of bromine and ether, and the bottle is frequently shaken for two hours; during this time bromine fumes must be plainly visible. The mass is then digested for 2 hours with 50 c.c. of water, the solution is filtered and concentrated to one-fifth of its bulk, and a little bromine water and then an excess of stannous chloride added, which will then give the usual reaction. One part of gold in 2,000,000

parts of ore may be thus detected. Tellurium interferes with the test.

L. DE K.

Detection of Benzene in Denatured Alcohol. By GEORGES HALPHEN (*J. Pharm.*, 1900, [vi], 11, 373—375).—The alcohol is mixed with brine and extracted with carbon disulphide, which dissolves the benzene. The carbon disulphide extract is then treated with a mixture of Nordhausen sulphuric acid and fuming nitric acid. The acid layer which now contains the benzene as nitrobenzene, is separated, mixed with water, and extracted with ether. The ethereal extract is evaporated, and the residue reduced with zinc dust and dilute hydrochloric acid. The solution is next filtered, and a few drops of a solution of sodium nitrite added to the filtrate, which is then neutralised with sodium carbonate. An alkaline solution of α -naphthol is finally added, when, if benzene is present, an orange-red coloration will be produced.

H. R. LE S.

Hundertkräuter-Likör (Centerba). By GIULIO PARIS (*Zeit. Unters. Natur.-Genussm.*, 1900, 3, 153—158).—This liqueur, prepared in the Abruzzi, occurs mainly in two forms, the *potabile*, which is sweet, and the *semplice*, which is more strongly alcoholic and is not sweet. The author has estimated the alcohol, free acid, total solids, ash, esters, fusel oil, sucrose, and glucose in several specimens of each variety obtained direct from the factories. Of the *centerba semplice* there appear to exist two varieties, one of which is coloured green by chlorophyll, and is prepared by extracting aromatic herbs with alcohol; the other is coloured with artificial dyes. M. J. S.

Some Properties of Glycerol. By HEINRICH STRUVE (*Zeit. anal. Chem.*, 1900, 39, 95—99).—Commercial glycerol contains 6—8 per cent. of water. After drying over sulphuric acid in a partial vacuum, it still retains 1.52 per cent. of water. After drying in this manner, it gains slightly in weight if exposed in a platinum crucible in the water oven, but at the same time a small loss of glycerol takes place (compare Abstr., 1899, ii, 816). Glycerol also volatilises in small amount when its aqueous solution is distilled (see Abstr., 1895, ii, 537). Dehydrated glycerol absorbs about 17 per cent. of water on exposure to the atmosphere. Some of the author's conclusions are based on the sp. gr. of the glycerol (compare Abstr., 1899, ii, 64).

M. J. S.

[Estimation of Pentoses in Urine]. By SULEIMAN BEY (*Chem. Centr.*, 1900, i, 803—804; from *Zeit. klin. Med.*, 39, 305—312).—In order to determine the quantity of pentoses in urine, it is necessary to evaporate until the liquid contains 2—3 per cent., and then only 92 per cent. of the theoretical quantity is obtained by precipitating with twice the volume of alcohol. The barium dipentosates are also carried down with the barium glucosates, which have a different composition, and it is impossible to isolate the sugar in this way from a urine containing 0.75 per cent. of xylose. The phloroglucinol and orcinol reactions of the pentoses are not distinguishable in presence of large quantities of glucose, but in such cases the pentoses may be estimated by separating as the barium compounds, and fermenting.

In reference to the use of phenylhydrazine in fermentation experiments, it is to be noted that mixtures of pentosazone and glucosazone often show a higher melting point than that of glucosazone alone.

Since rhamnose does not form a barium compound which can be precipitated by alcohol, it may be readily separated from the pentoses, but it cannot be detected by the orcinol or phloroglucinol reactions in the presence of comparatively small quantities of xylose. Xylose and rhamnose may be estimated in a mixture by first determining the reducing power of both sugars, and then precipitating the xylose in another portion, and determining the reducing power of the filtrate after removing the barium and alcohol. The results obtained are, however, 1—2 per cent. too high for the rhamnose. In separating arabinose and rhamnose, the greater solubility of barium di-arabinoxylate in alcohol prevents the complete precipitation of this compound.

E. W. W.

Analysis of Golden Syrup. By NORMAN LEONARD (*Analyst*, 1900, 25, 85—87).—The author replies to the criticism of Bodmer, Leonard, and Smith's process (this vol., ii, 320) by Miller and Potts (*ibid.*), and states that their suggested improvement is not suited so well for the wants of public analysts as the process given by himself and colleagues.

L. DE K.

Treacle or Golden Syrup. By EDWARD W. T. JONES (*Analyst*, 1900, 25, 87—89).—The author suggests the following simple formula for arriving at the percentage of glucose syrup in a sample of golden syrup if this has a *dextro*-rotation *after inversion*.

$$[a]_f \frac{([a]_f \text{ after inversion} + 12.3) 100}{133.3} = \text{per cent. of glucose syrup.}$$

$$[a]_D \frac{([a]_D \text{ after inversion} + 11) 100}{120} = \text{per cent. of glucose syrup.}$$

A sample of commercial golden syrup declared to contain 18 per cent of glucose syrup had a specific rotation *after inversion* of $[a]_f + 12.3$ or $[a]_D + 11.07$ therefore by the above formula it shows 18.4 per cent.

The method of working is as follows. A 10 per cent. solution is made at 15.5°, and its sp. gr. taken. This should not be less than 1.032, indicating 20 per cent. of water. The factor, 3.86, is correct for about 10 per cent. solution of pure sucrose, but when dealing with ordinary golden syrups, the amount of water thus found is too low to the extent of about 3 per cent. The solution is now heated to 17.5°, and examined in the 10 cm. tube. Fifty c.c. of the same solution are heated with 5 c.c. of normal acid in a 100 c.c. flask in boiling water for 20 minutes, cooled, mixed with 5 c.c. of normal soda, and then diluted to 100 c.c. at 15.5°. This solution is again polarised at 17.5° and the result multiplied by 2.

For the cupric reducing power, if required, 10 c.c. of the first solution is taken and diluted to 100 c.c.; 20 c.c. of this is added to 50 c.c. of Fehling's solution diluted with 30 c.c. of water which has been standing for some time in boiling water. After 12 minutes, the cuprous oxide is collected, washed, and gradually ignited in a porcelain

crucible to convert it into oxide, from which the amount of sugar corresponding is calculated. Of the inverted solution, 20 c.c. are diluted to 100 c.c., and of this 20 c.c. are treated in the same manner; the difference in copper oxide represents cane sugar. L. DE K.

Analysis of a Sample of Treacle and of so-called Golden Syrup. By CHARLES G. MATTHEWS and A. HYDE PARKER (*Analyst*, 1900, 25, 89—94).—The process adopted by the authors consists in taking the sp. gr. of a 10 per cent. solution of the sample, and making a due allowance for the ash. The usual factor, 3.86, is then used for calculating the organic solid matter. Cane sugar is estimated by polarising the solution as usual after a partial fermentation with yeast at 52° for 5 hours, and boiling to destroy birotation. The cupric reducing power is taken by the gravimetric method on 0.1 gram of the sample. The rotation and cupric reducing power are also taken after fermenting for 72 hours at 18°. When analysing commercial golden syrup, a determination is also made of combined dextrin (amyloindextrin), by treating of the fermented solution with cold water malt extract, and noticing the increase in cupric reducing power, but as a further fermentation on adding yeast does not take place to any appreciable extent, the authors do not think themselves justified in using the figures so obtained for dextrin.

Using a Soleil-Ventzke-Scheibler apparatus, the value of a 1 per cent. solution of the substance observed in a 20 cm. tube has been taken to be: for maltose, 8.02 divisions; for dextrin, 11.56; for dextrose, 3.05; for gallisin, 4.85; and for cane sugar, 3.84. These figures may be converted into Laurent degrees by multiplying by 0.344.

The cupric reducing power for maltose has been taken as 1.37; for dextrose, as 2.46; and for gallisin, as 1.01. L. DE K.

The Unrestricted Use of Starch Syrup in Articles of Food. By JOSEF KÖNIG (*Zeit. Unters. Nahr.-Genussm.*, 1900, 3, 217—221).—In Germany, the employment of starch-sugar, or syrup in articles of food without declaration is prohibited, but in view of the harmlessness of these products and the advantageous results which they afford in certain confections, the question has been raised whether this restriction is called for. The presence of dextrin in these articles, and especially in the syrup, confers on them a viscosity which enables them to take the place of stronger solutions of cane sugar, and in consequence of the hindrance which the presence of 5—10 parts of starch syrup in 100 parts of cane sugar opposes to the crystallisation of the latter, enables them in part to replace fruit juice itself. The author has made comparative estimations of the viscosity of solutions of cane sugar, starch sugar, and starch syrup, both with Engler's viscosimeter and with Weiss' "consistence measurer," and gives the preference to the latter, both from its convenience in use, and from the fact that when the retardation of the revolutions is calculated for a unit weight of substance, the results are almost independent of the concentration of the solution, which is by no means the case with the viscosimeter.

M. J. S.

Estimation of Cellulose. By CARL BECK (*Zeit. Unters. Nahr. Genussm.*, 1900, 3, 158—164).—Upwards of 45 methods of estimating

cellulose in vegetable structures have been proposed. That of Henneberg and Strohmann, which for 30 years has been generally accepted, consists in boiling the substance with dilute sulphuric acid (1.25 per cent.) and then with potassium hydroxide of corresponding strength. Lebbin (*Arch. Hyg.*, 1897, 212) suggested the use of a mixture of hydrogen peroxide and ammonia, and König (Abstr., 1899, ii, 68) has proposed heating under certain defined conditions with a mixture of glycerol and sulphuric acid, the special object being the removal of pentosans. The author has made comparative estimations in cotton-wool, filter-paper, straw, wood-wool, wheat-bran, pearl barley, and wheat flour, by the three methods, as well as by a modification of Lebbin's method (which is not described because the author himself does not recommend it), and concludes that Lebbin's process has neither a scientific nor a practical value; that in König's method (with a reflux apparatus) it is difficult to maintain the exact temperature prescribed, and that the results obtained with a small gas flame are higher than those with a large flame. Finally, that Henneberg's process gives the most concordant results, and is, on the whole, the most trustworthy. König's reagent attacks cellulose itself strongly; nevertheless, his process gives higher numbers than Henneberg's with bran and flour.

M. J. S.

[Estimation of Cellulose.] By JOSEF KÖNIG (*Zeit. Unters. Nahr. Genussm.*, 1900, 3, 164—166).—The discordant results obtained by Beck with the author's process are due to the irregularity of the temperature of boiling. If the instructions are carefully complied with and a small flame is used, the temperature will only vary between 131° and 133°, and should never be allowed to exceed the latter.

M. J. S.

Isolation and Separation of the Chief Organic Acids. By N. SCHOORL (*Zeit. angew. Chem.*, 1900, 367—370).—The process is based on the fact that formic and acetic acids may be distilled in a current of steam after acidifying the liquid to be tested with sulphuric acid, congo test-paper serving as indicator.

The residue, after being concentrated on the water-bath, is extracted in a suitable apparatus with ether, which rapidly dissolves salicylic, benzoic, succinic, and lactic acids, and gradually removes oxalic, malic, citric, and even tartaric acids.

The ether is then evaporated and the residue treated with boiling water, which, on cooling, deposits most of the salicylic and benzoic acids. The further separations present, on the whole, no novel features. The microscope renders good service in the recognition of calcium citrate or zinc lactate.

L. DE K.

Estimation of Formic Acid in Presence of Acetic Acid. By FIN SPARRE (*Zeit. anal. Chem.*, 1900, 39, 105—106).—The author recalls and strongly advocates the method of Portes and Ruyssen (Abstr., 1876, ii, 663), but points out that the instruction to employ a 10 per cent. solution of the substance must be a misprint for 1 per cent., since the quantity of mercuric chloride prescribed is not sufficient for the stronger solution, and with solutions containing more than 1 per cent. of formic acid the results are too high.

M. J. S.

Cider Vinegar: Its Solids and Ash. By R. E. DOOLITTLE and WILLIAM H. HESS (*J. Amer. Chem. Soc.*, 1900, 22, 218—220).—Pure cider vinegar may be distinguished from spurious vinegar (generally made from dilute acetic acid) by the fact that the solids consist of glycerol, albuminous matters, gums, malic and other organic acids and mineral matters, give no rotation in the polariscope and have little or no cupric reducing power after the usual clarification with lead acetate. On the other hand, the spurious vinegars leave generally a residue of molasses-like appearance and properties.

The ash of cider vinegar, which should amount to not less than 0.25 per cent., contains principally potassium, with small amounts of aluminium, calcium, magnesium, and sulphuric and phosphoric acids, with variable amounts of carbon dioxide, but its chief characteristic is the complete absence of sodium. Spurious substitutes often contain a large proportion of either calcium or sodium.

Analyses are given of the solids and the ashes of cider, cider vinegar, and spurious samples.

L. DE K.

Estimation of Uric Acid in Urine. By ADOLF JOLLES (*Zeit. physiol. Chem.*, 1900, 29, 222—248).—By boiling with an excess of permanganate in a solution acidified with sulphuric acid, uric acid is quantitatively converted into urea, which can then be estimated by the hypobromite process. The urine (50—200 c.c. according to concentration), which, if necessary, must be warmed to dissolve urates and be filtered if turbid, is treated with solid ammonium acetate (1 gram per 10 c.c.) and made feebly alkaline with ammonia. After $2\frac{1}{2}$ —3 hours, the ammonium urate is collected on a filter, and washed free from chlorides with a saturated solution of ammonium carbonate. It is then rinsed into a beaker and boiled with 0.1—0.2 gram of pure magnesia for $\frac{1}{2}$ — $\frac{3}{4}$ hour, or until perfectly free from ammonia. The liquid, measuring 300—400 c.c., is then acidified with 10 c.c. of sulphuric acid (sp. gr. 1.4) and permanganate solution (8 grams per litre) is gradually added, until the last c.c. remains unreduced after 15 minutes boiling. The excess of permanganate is removed by oxalic acid, the liquid cooled, rendered alkaline with soda, and transferred to the reaction vessel (330 c.c. capacity) of a special azotometer, where it is treated with hypobromite. Test estimations, with pure uric acid, gave excellent results. When applied to urine, the results were compared with those of the Ludwig-Salkowski process (*Wien. med. Jahrbuch*, 1884, 97), which the author affirms to be trustworthy and exact, but which is admitted by Ludwig to give numbers which are 2 per cent. too low. With a number of normal and pathological urines, the differences ranged from -1.9 to +5.0 per cent., the average difference being 2 per cent. above the Ludwig-Salkowski numbers. The present method may, therefore, be regarded as one of the most exact. The Hopkins-Folin method (*Abstr.*, 1898, ii, 196), which gives accurate results with pure uric acid, is liable to give excessively high numbers with certain pathological, and especially with highly concentrated, urines.

M. J. S.

Estimation of Fat in Dairy Produce. By LÉON LINDET (*J. Pharm.*, 1900, [vi], 11, 368—373. Compare this vol., i, 67).—This

method is based on the fact that a hot solution of resorcinol dissolves the casein from milk, cheese, &c., and leaves the fat as a supernatant layer, which is easily distinguished from the lower layer if the milk has been previously coloured with a little magenta. If the milk is rendered faintly alkaline with sodium hydroxide, the casein is readily dissolved by simply heating the mixture in boiling water. Five grams of resorcinol, 5 c.c. of the milk, 2 drops of a solution (36°) of sodium hydroxide, and 1 drop of the colouring solution are heated in a special form of graduated tube, and the volume of the separated fat is read off. One gram of butter fat at 15° occupies 1.154 c.c. In the case of cheese, 1 gram of the substance and 15 c.c. of a hot, aqueous 100 per cent. solution of resorcinol are the quantities employed. The method is rapid, and gives accurate results.

H. R. LE S.

Sour Milk. By H. DROOP RICHMOND and J. BRISTOWE P. HARRISON (*Analyst*, 1900, 25, 116—124).—The first part of the paper is devoted to an investigation of the fact noticed by de Koningh (*Abstr.*, 1899, ii, 707) that milk, on being mixed with 5 per cent. of a solution of sodium hydroxide of the same sp. gr., suffers a diminution in sp. gr. The authors confirm this fact, but state that it depends on the state of acidity of the milk, because when lactic (or, in fact, any other) acid is neutralised with solution of soda, the resulting sp. gr. is less than the calculated sp. gr. If, however, ammonia is used for neutralisation, the resulting sp. gr. is practically the same as the calculated one. Tables are given showing the loss in sp. gr. when various acids are neutralised with soda, and of the slight increase noticed when ammonia is used.

Owing to this fact, the authors think that ammonia is the best alkali for the purpose of liquefying sour milk so as to be able to take its sp. gr. with a hydrometer. This idea is not novel, having already been proposed in 1893 by Weibull, but the authors have much simplified the process by mixing pure milk with 5 per cent. by volume of a strong ammonia, and noticing once for all the decrease in sp. gr. which takes place. Sour milk is then treated in the same manner, and the loss caused by the ammonia is allowed for. If the operator prefers using de Koningh's process (*ibid.*), the loss in sp. gr. will be 0.02 for every degree of lactic acid. It must be borne in mind that the acidity of milk is not entirely due to lactic acid; in fact, fresh milk, which is fairly neutral to litmus paper, still shows an acidity of about 20° manifested towards phenolphthalein.

The second part of the paper is devoted to the point at which milk may be considered to be sour, and the rate of souring in the presence or absence of preservatives. The figures as to the degree of acidity necessary to cause the coagulation of milk on boiling confirm the previous experiments of Stokes, who stated that milk is sour when the acidity reaches 44°.

Tables are given showing the retardating action of formaldehyde and boric preservative on the formation of the additional acidity.

L. DE K.

Foreign Colouring Matter in Milk. By ALBERT E. LEACH (*J. Amer. Chem. Soc.*, 1900, 22, 207—210).—150 c.c. of the sample

are heated in a casserole and curdled by means of acetic acid. The curd is, if possible, gathered in one mass, and the whey poured off; or, if the curd is finely divided, the mass is strained. The pressed curd is macerated in a corked flask with ether, which is then poured off and evaporated. The residual fat is treated with aqueous sodium hydroxide, which is then passed through a wetted filter; the fat is washed off the filter and the latter is dried, when, should it have an orange colour, the presence of annato is indicated, which may be further confirmed by the pink colour produced in contact with stannous chloride.

If the extracted curd is colourless, it has no other foreign colour, but if orange or brownish, it may contain aniline-orange, or caramel. It is then shaken in a test tube with strong hydrochloric acid; should it immediately turn pink, aniline-orange is present, but if it turns gradually blue, it indicates caramel, which may be confirmed by the usual tests applied to the whey.

L. DE K.

Butters from Various Countries Compared. By CHARLES ESTCOURT (*Analyst*, 1900, 25, 113—116).—This is a tabulated record of the analysis of some 250 samples of butter imported from Finland, Denmark, Iceland, Sweden, Canada, and Germany. The testing was restricted to the percentage of water, the Reichert figure, and search for preservatives.

The results given by the Reichert process varied from 11.9 to 16 c.c. of decinormal alkali. The preservative found in a few foreign samples consisted of boric acid to the extent of about 8—9 grains per pound, but of the 39 samples of Irish butter 35 contained boric acid to the extent of 5—46 grains per pound. The highest percentage of water met with was 20 per cent.; the lowest 8 per cent.

L. DE K.

Detection of "Process" or "Renovated" Butter. By WILLIAM H. HESS and R. E. DOOLITTLE (*J. Amer. Chem. Soc.*, 1900, 22, 150—152).—"Process" or "renovated" butter is an article prepared by melting rancid butter and mixing the clarified fat with milk. The method given for the identification of such butter is based on the fact that the curd from cream such as exists in genuine samples of butter is physically and chemically different from curd derived from milk.

When the curd of a sample of "process" butter is separated by washing with ether, and then spread out in a thin layer on a clean glass plate, its physical appearance when viewed with a magnifier of 3—6 diameters is quite distinct from that obtained from genuine butter. The latter has an amorphous, non-granular appearance, whilst the curd of the former has a very coarse, curdy appearance. The curd from cream is a gelatinous, ropy mass, which settles rapidly, but the other is a granular, easily divided substance. Casein dissolves readily in acid or alkali; the curd of genuine butter only dissolves on prolonged treatment with these reagents. The curd of pure butter yields scarcely any albumin to water, but when the curd from milk, after thorough washing with ether, is treated with water, the filtrate coagulates on adding acetic acid and boiling. By means of the Kjeldahl process, the relation between casein and albumin may be

readily estimated, and in samples containing only the curd of milk this amounts to 9 : 1.

L. DE K.

Comparison of some Tests for Formaldehyde. By BENJAMIN M. PILHASHY (*J. Amer. Chem. Soc.*, 1900, 22, 132—135).—Schiff's reagent, magenta decolorised by sulphurous acid, is not a trustworthy test, as the violet coloration is also obtained by the action of the air or by warming the suspected liquid. The scarlet ring noticed when liquids containing formaldehyde are poured on to sulphuric acid containing a little phenol is also produced by most other aldehydes. The same may be said of the violet colour produced by diazobenzene-sulphonic acid in the presence of free alkali and sodium amalgam. Nessler's solution, and also aniline, give a precipitate both with formaldehyde and acetaldehyde.

The author has proved that Trillat's dimethylaniline test does not show the presence of formaldehyde, but is due to the dimethylaniline itself, or of its salts when these are not completely volatilised.

Lebbin's test is supposed to detect 1 part of formaldehyde in 10,000,000 parts of water, but the author states that 1 in 200,000 is the limit. The purple ring formed by bringing the liquid in contact with a solution of morphine hydrochloride in sulphuric acid is no longer distinct if the dilution of the formaldehyde exceeds 1 : 1000.

A solution of 1 gram of phenylhydrazine hydrochloride and 1.5 grams of sodium acetate in 10 c.c. of water seems to be the best reagent. To 1 c.c. of the liquid 2 drops of the reagent and 2 drops of sulphuric acid are added, producing a green coloration. When the dilution is 1 : 10,000 or 1 : 100,000, 3 c.c. of the liquid, 4 drops of the reagent, and 4 drops of sulphuric acid are used, and the mixture is heated for half a minute. In case of a dilution 1 : 250,000, 3 c.c. of the liquid are heated for about a minute with 5 drops of the reagent and 5 drops of sulphuric acid, when a very light tinge of green will be noticed after 3 minutes, and a decided tint after 10 minutes.

Another delicate test has been proposed by Rimini: 1 c.c. of the liquid is mixed with 2 drops of solution of phenylhydrazine hydrochloride, 2 drops of solution of sodium nitroprusside, and 1 c.c. of aqueous sodium hydroxide. A blue colour is developed, which changes quickly to green, yellow, light brown, and red; a peculiarity is the rise of the red colour to the top, leaving a yellow layer below. The limit for this test seems to be reached when the dilution is as 1 : 1,000,000.

L. DE K.

Two Deceptive Reactions. By CARL AMTHOR (*Zeit. Unters. Nahr.-Genussm.*, 1900, 3, 233—235).—The violet colour observed by Leonard and Smith (*Abstr.*, 1899, ii, 454) when milk containing formaldehyde is heated with fuming hydrochloric acid, and by Fisher with milk to which boric acid has been added, is obtainable with normal milk, and is a reaction of albuminous substances in presence of sugar. With sour milk from which most of the sugar has disappeared, or with muscular tissue or egg-albumin, the reaction is feeble, but in all these cases it is given strongly after adding lactose. The

colour may also be obtained with butter if new and used in the unfiltered state, in consequence of the presence of both casein and lactose. With old butter, the reaction is only observed after adding some lactose. It is producible in the cold, but more strongly on heating, and appears to be due to the formation of furfuraldehyde by the action of the acid on the sugar present. It is, in fact, immediately obtained with unfiltered butter to which some furfuraldehyde is added. The furfuraldehyde test for sesamé oil is therefore quite untrustworthy if applied to butter which has not, by filtration or by dissolving in ether, been completely freed from proteids (compare this vol., ii, 325). M. J. S.

Colour Reaction of Acetaldehyde. II. By ENRICO RIMINI (*Gazzetta*, 1900, 30, i, 279—281).—The colour reactions obtained by Lewin (this vol., ii, 179) by the addition of a secondary amine and sodium nitroprusside to either acetaldehyde or propionaldehyde were described in earlier papers by the author (this vol., ii, 56, and *Rendiconti Amministr. Civile. Ministero del Interno*, 1898). As stated by Simon (*Abstr.*, 1898, ii, 315), no reaction is obtained with carefully purified paraldehyde. T. H. P.

Physico-chemical Properties of Chloral Hydrate and their Applications to Pharmacology. By RICHARD MAUCH (*Zeit. anal. Chem.*, 1900, 39, 116—131; from *Diss. Strassburg*, 1898).—The author greatly extends Schaefer's observations (this vol., ii, 57) on the solvent powers of strong (60—80 per cent.) solutions of chloral hydrate and chloral alcoholate. With few exceptions, the reactions of the alkaloids can be well observed with their chloral hydrate solutions. Most resins and gum resins, camphors, tannins, organic dyes, sugars, dextrans, gelatin, and keratin are also freely soluble. The dammar resins from dipterocarpous trees are almost insoluble, whilst those from *Coniferae* dissolve completely. Many reactions of solutions of gum-resins and balsams are described in the paper. M. J. S.

Vanillin in Wine Vinegar. By A. STOCKY (*Zeit. Unters. Nahr.-Genussm.*, 1900, 3, 235).—In two samples of commercial vinegar, a substance was detected having the odour of vanillin. The acid was evaporated with calcium carbonate, the residue extracted with ether, and the residue from the evaporation of the ethereal extract crystallised from alcohol. It reduced ammoniacal silver solution, and gave Etti's phloroglucinolvanillin (Abstr., 1883, 62). M. J. S.

[Estimation of Carvone in Essential Oils.] By HENRI LABBE (*Bull. Soc. Chim.*, 1900, [iii], 23, 280—286).—See this vol., i., 398.

A Quantitative Reaction of Ureides and Purine Derivatives. By ADOLF JOLLES (*Ber.*, 1900, 33, 1246—1248).—A number of ureides and purine derivatives are not oxidised directly to ammonia by potassium permanganate and sulphuric acid, but give a quantitative yield of carbamide, provided that the weight of acid does not exceed 40 grams per litre. After removing the excess of permanganate with oxalic acid, neutralising with alcoholic potash, and evaporating nearly to dryness, the carbamide can be extracted from the inorganic salts with

absolute alcohol, precipitated with ethereal oxalic acid, and the oxalate analysed in the usual way.

The nitrogen is completely converted into carbamide in the case of alloxan, alloxantin, allantoin, uric acid, and xanthine. In hypoxanthine, adenine, and guanine, 1 atom of nitrogen appears in the form of guanine, and the remaining 4 atoms as urea. T. M. L.

[Estimation of Nicotine in Cigars.] By HERMANN THOMS (*Chem. Centr.*, 1900, i, 826—827; from *Ber. Deut. pharm. Ges.*, 10, 19—31).—See this vol., ii, 428.

Strychnine Salts and Chloroform. By J. RUTHERFORD HILL (*Pharm. J.*, 1900, [iv], 10, 185).—Normal salts of strychnine are not quite insoluble in chloroform. One part of the hydrochloride dissolves in 169 parts of chloroform, the arsenate requires 1178 parts, and the sulphate 1055 parts; but in the case of the arsenate and sulphate the portion dissolved is no longer the pure normal salt, but contains free alkaloid.

When aqueous solutions of these salts are shaken with chloroform, the latter abstracts a small amount of the hydrochloride as such, particularly in the presence of hydrochloric acid, but with the two other salts a notable amount of alkaloid is abstracted, leaving the liquid correspondingly acid. The only way to prevent even traces of strychnine from passing into the chloroform is to add a fair excess of sulphuric acid. L. DE K.

Action of Chloroform and Similar Solvents on Alkaloid Salts. By EDWARD SCHAEER (*Pharm. J.*, 1900, [iv], 10, 308).—The author is continuing Hill's researches (preceding abstract).

Experiments already made with atropine and veratrine have shown that their acid salts are also soluble in ether or chloroform. 0.102 gram of atropine dissolved in water acidified with tartaric acid yielded 0.0623 gram to 30 c.c. of chloroform and 0.0913 to the same quantity of ether. Veratrine dissolved in solution of tartaric acid yielded to chloroform an amount of veratrine tartrate varying with the quantity of free acid present. L. DE K.

Examination of Tea. By ADOLF BEYTHIEN, PAUL BOHRISCH, and JOSEPH DEITER (*Zeit. Unters. Nahr.-Genussm.*, 1900, 3, 145—153).—An attempt to estimate the extractive matter in tea by Trillich's method, which consists in taking the specific gravity of an extract obtained by boiling 10 grams of tea with 250 grams of water for 15 minutes, gave results about 10 per cent. below those yielded by complete exhaustion. In consequence of the bulkiness of boiled tea-leaves and the slowness with which they yield up their extractive matter, 5 grams of tea requires four boilings with 750 c.c. of water each time to extract it completely. The extract should not be evaporated, but the exhausted leaves be dried and weighed, allowance being made for the moisture in the original substance. Identical results are obtained by a percolation method, in which the tea, supported in a tube on cotton-wool, is exposed for 8—10 hours to the percolation of condensed steam from the receiving flask, but when numerous samples have to be examined the following method gives good results with very little

trouble : 3 grams of the tea are placed on a circular piece of linen, which is then drawn together, so as to form a small bag ; 8 to 10 of these bags, each weighted with a numbered piece of lead, are suspended in an enamelled saucepan full of water, which is kept boiling, and is changed for fresh water either intermittently or continuously. When the decoction is no longer coloured, the bags are spread open, dried, and the exhausted tea-leaves transferred to watch-glasses. The extraction by this method requires 3 or 4 days.

The examination of 130 samples of tea, purchased in Dresden, showed, in 100 parts :

	Extractive matters.	Ash.	Ash soluble in water.	Percentage of ash soluble in water.
Mean	35.03	5.78	3.13	54
Minimum ...	29.53	5.32	2.08	33
Maximum ...	44.75	6.40	3.99	68

All the samples appeared to be perfectly genuine.

M. J. S.

Testing Antipyrin for Antifebrin, Phenacetin, and Exalgin. By P. N. RAIKOW and P. SCHATBANOW (*Chem. Centr.*, 1900, i, 999 ; from *Oesterr. Chem. Zeit.*, 3, 125—127).—By boiling with phosphoric acid of sp. gr. 1.7, in which these substances are soluble, the anilides antifebrin and phenacetin are hydrolysed and yield acetic acid free from bye-products, so that very small quantities may be recognised. Antipyrin colours the phosphoric acid golden-yellow, which gradually becomes darker and brownish-yellow. Antifebrin gives a pale yellow colour, turning brown on prolonged boiling. Phenacetin causes first a rose, then a brownish-red coloration, passing from reddish-violet, through violet and bluish-green into dirty green. The appearance of the violet colour is particularly characteristic for phenacetin.

Antifebrin and phenacetin are distinguished by their behaviour towards potassium hydroxide. A few grams of the substances are heated with 2—4 c.c. of strong aqueous potash in a test-tube closed by a perforated india-rubber cork, through which passes a bent tube dipping into another test-tube containing 1 to 3 c.c. of a clear solution of bleaching powder. In the presence of antifebrin, the first drops which distil over cause the well known violet colour due to aniline. In the absence of antifebrin and the presence of phenacetin, the first drops cause no colour, but those following give a vermilion-red turbidity, due to phenetidine ; finally, an amorphous, red substance separates on the surface of the liquid, which becomes clear yellow after some time. If the test-tube is changed, both the reactions, the violet colour and the separation of phenetidine may be noticed in succession. When boiling a mixture of phenacetin and antipyrin with potassium hydroxide, the distillate does not give with bleaching powder the characteristic red coloration for phenacetin, but the solution turns first yellowish-green and then yellowish-grey, whilst with antipyrin alone it remains colourless.

Exalgin readily evolves acetic acid when boiled with phosphoric acid, and the liquid turns golden-yellow. The separated methylaniline distils in oily drops, which collect on the surface of the bleaching

powder solution, and soon become green, then greyish-green, and finally dirty brown. Contrary to Fischer's statement, exalgin is easily hydrolysable by caustic alkalis.

When boiled with aqueous potash, quinine gives no volatile products which act on bleaching powder solution. When boiled with phosphoric acid, the liquid turns first yellow, and shows an intense yellow, bluish-green fluorescence; it then soon becomes dirty brown and opaque. The presence of anilides in quinine may be safely detected by this method.

Traces of *p*-aminophenol may be detected in phenacetin, antifebrin, &c., by the intense red colour developed when dissolving these substances in cold phosphoric acid. When pure, they dissolve to a colourless liquid.

L. DE K.

Analysis of Tanning Materials. By PAESSLER (*Zeit. angew. Chem.*, 1900, 318—323).—Attention is called to the fact that, in order to get trustworthy commercial results, directions issued by the "International Committee of Leather Trades Chemists" must be scrupulously followed. The merest deviation from those instructions may cause a difference of several per cent. in the amount of tannic acid found.

L. DE K.

Distinction of Indigo from other Blue Dyes on Fabrics. By FREDERIK H. VAN LEENT (*Zeit. anal. Chem.*, 1900, 39, 92—95).—Indigo is readily soluble in hot phenol, and woollen fabrics dyed with indigo alone can be deprived of the dye completely by heating with that solvent in the water-bath. At higher temperatures, the fabrics are attacked. Other blue dyes except indophenol are wholly or partially unattacked, the wool remaining coloured. From cotton, indoin is dissolved as well as indigo.

M. J. S.

Rosin's Method for the Determination of the Reducing Power of Urine, &c. By SPIEGEL and PERITZ (*Chem. Centr.*, 1900, i, 675; from *Münch. Med. Wochschr.*, 47, 225—226).—The authors have arrived at the conclusion that Rosin's method with leucomethylene-blue (this vol., ii, 319) is quite untrustworthy as it is influenced by the temperature, and by other constituents of urine such as uric acid, whilst, moreover, the reducing power of the various reducing substances is not a quantitative one.

L. DE K.

[Cystine in Impure Well Waters in the Neighbourhood of Lyons.] By HENRI CAUSSE (*Compt. rend.*, 1900, 130, 579—581).—Impure well waters which had caused typhoid were found to contain cystine, probably in the form of ferric cystinate. The waters gave a yellow coloration with sodium *p*-diazobenzenesulphonate mercurichloride, weakened, but not discharged, by addition of sulphurous acid; when boiled for some time, they gave off hydrogen sulphide, free sulphur being precipitated at the same time. The cystine was isolated by precipitation with a solution of barium hydroxide containing some barium chloride, and its identity was established by recognition of its crystalline form, by determinations of the ratios C:N and Fe:S, and by its reactions with lead, silver, and mercuric salts.

The typhoid bacillus could not be isolated from the waters in

question, but they contained an abnormally large number of bacteria that liquefy gelatin, and especially of *Bacterium termo*. C. H. B.

Detection and Estimation of Cystine, and its Variation in Amount in Contaminated Water. By HENRI CAUSSE (*Compt. rend.*, 1900, 130, 785—788. Compare preceding abstract). — The reagent employed in testing for cystine in natural water is prepared by adding mercuric chloride to a solution of sodium sulphanilate, and dissolving the mercurichloride thus produced in a solution of sodium chloride. The water under examination is shaken with a few c.c. of this reagent, a few drops of dilute hydrochloric acid and potassium nitrite solution are added, and the mixture left for 6 hours in a dark place. The yellow coloration which develops in water free from cystine is entirely destroyed by sulphurous acid. The orange colour of the meniscus persists when traces of cystine are present, and in the presence of larger quantities of this substance the whole of the liquid retains its colour, and the meniscus is red.

The colorimetric estimation of cystine in water is effected by comparing the tint which persists after the addition of sulphurous acid with that obtained in a similar manner with standard solutions of cystine.

Analyses of the potable water of Lyons show that there is an intimate connection between the accumulation of cystine in the water and the outbreak of typhoid fever.

The amount of cystine in well water varies with the seasons; it is at its minimum in February and March, and reaches its maximum at the close of the summer; this is also true of the water from the Rhone; under ordinary circumstances, water from the latter source contains far less cystine than well water, but when the river is in flood, the amount of this substance greatly increases. G. T. M.

Presence of Tyrosine in Contaminated Well Waters. By HENRI CAUSSE (*Compt. rend.*, 1900, 130, 1196—1198. Compare preceding abstracts). — Tyrosine is present in contaminated well waters, which give a yellow coloration on the addition of the reagent composed of mercuric chloride and sodium *p*-diazobenzenesulphonate. The tyrosine is not originally present in the water, but results from the subsequent oxidation of the inorganic and organic constituents in the water. It was isolated either by precipitation with Millon's reagent (slightly modified) or with barium hydroxide solution.

H. R. LE S.

The Ferricyanide Method of Determining the Oxygen Capacity of Blood. By JOHN S. HALDANE (*J. Physiol.*, 1900, 25, 295—302). — When the fallacies due to incomplete laking of the blood and to the presence of bacteria are eliminated, the ferricyanide method of determining the oxygen capacity of the hæmoglobin in blood gives exact results. The present paper deals with the precautions to be taken to attain these objects; the most important modification introduced is the substitution of ammonia for sodium carbonate to prevent the evolution of carbon dioxide, the advantage being that laking is more readily produced. W. D. H.

Simultaneous Estimation of Two Colouring Matters in Blood by the Spectrophotometer. By GUSTAV HÜFNER (*Chem. Centr.*, 1900, i, 512—513; from *Arch. anat. Phys.*, 1900, 39).—The ratios of the luminosity of different regions of the absorption spectrum of alkaline solutions of the blood-colouring matters are constant, even in the blood of different animals. Thus, with oxyhæmoglobin, the ratio of ϵ_0 , the extinction coefficient of the darkest part of the broader absorption band, 531·5 to 542·5 $\mu\mu$, to ϵ_1 ; that of the bright portion, 554—565 $\mu\mu$, between the two bands, is 1·578. Similarly, with reduced hæmoglobin, the value ϵ'_r/ϵ_r , in which ϵ'_r and ϵ_r are the extinction coefficients respectively of the same regions = 0·762. In mixtures of both oxyhæmoglobin and hæmoglobin, the equation $157·8 - (100 \cdot \epsilon'_e/\epsilon_e)/(0·529 \cdot \epsilon'_e/\epsilon_e) + 0·414 = x$, the percentage of hæmoglobin; $100 - x$ is the percentage of oxyhæmoglobin. To ascertain the absolute amount of the two colouring matters, the mixture is shaken with air, and the amount of oxyhæmoglobin estimated. For a mixture of methæmoglobin and oxyhæmoglobin, the fraction becomes $x = 157·8 - (100 \cdot \epsilon'_e/\epsilon_e)/0·393$, in which x is the percentage of methæmoglobin, and for one of carboxy-hæmoglobin (x) and oxyhæmoglobin, $\epsilon'_e/\epsilon_e = 157·8 + 0·061 \cdot x/100 + 0·497 \cdot x$. The original paper contains tables for these values. M. J. S.

Estimation of Absorbable Proteids in Foods. By KARL BÜLOW (*Chem. Centr.*, 1900, i, 831—832; from *J. Landw.*, 48, 1—38).—The greatest amount of proteids which can possibly be attacked are dissolved by treating foods or fæces by pepsin according to Kühn's method; some of the undissolved nitrogen is still soluble in alkaline trypsin solution. Excessive drying renders a portion of the proteids insoluble, and the temperature employed should not exceed 55—60°.

The Stutzer-Pfeiffer method for estimating digestible proteids does not yield results in accordance with those of experiments with animals. Treatment of foods with pepsin-trypsin gives numbers which are too high, whilst the action of as little as 250 c.c. of pepsin solution on fæces does not dissolve all the nitrogen soluble in acid pancreatic juice.

Kühn's method is suitable for estimating proteids dissolved by the intestines, and is useful for rapidly ascertaining the amount of digestible proteids in foods; it does not, however, render direct experiments unnecessary. The correctness of the method is established as regards ruminants; further experiments are necessary to show whether it is available in the case of other animals.

N. H. J. M.

Sulphosalicylic Acid as a Test for Albumin [in Urine]. By MANKIEWICZ (*Chem. Centr.*, 1900, i, 630; from *Berl. Klin. Woch.*, 36, Litteraturauszüge, 93).—The urine, if turbid, is clarified by means of a little magnesium sulphate or sodium hydrogen carbonate; 10 c.c. of the clear filtrate are mixed in a test-tube with 0·1—0·15 gram of sulphosalicylic acid, and well shaken. In the presence of 0·001 per cent. of albumin, a faint bluish diffused coloration is noticed on placing the tube against a dark surface; if 0·005—0·01 per cent. is present, the turbidity is plainly opalescent, and when 0·02 per cent. is present, the liquid becomes quite opaque. L. DE K.

Examination and Valuation of Commercial Pastry.

By ADOLF JUCKENACK (*Zeit. Nahr. Genussmitt.*, 1900, 3, 1—17).—Artificial yellow dyes are added to commercial pastry to simulate the appearance of the use of eggs; they are, however, all soluble in 70 per cent. alcohol, but insoluble in ether, whilst lutein is soluble in both menstrua. Since yolk of egg is a residual product of certain industries, it is often used instead of entire eggs. The large proportion of cholesterol in yolk of egg renders its detection in pastry an almost certain proof of the presence of egg-substance. About 15 grams of the substance should be extracted with cold ether, the ether evaporated, the residue saponified with potash, the soap dissolved in 5 c.c. of water, and the solution shaken with ether. The crude cholesterol so obtained is extracted with chloroform; half of the chloroform solution is evaporated, and the residue crystallised from alcohol for microscopic examination; other portions are tested by Salkowski's and Liebermann's reactions.

For quantitative purposes, the phosphorus present in the form of lecithin and its compounds is estimated, since the proportion in egg so largely exceeds that in wheat flour. About 35 grams of the thoroughly dry substance is extracted with absolute alcohol in a Soxhlet apparatus at 55—60° for 10—12 hours. The matter soluble in alcohol is saponified with potash, and evaporated and incinerated in a platinum capsule. The phosphoric acid in the ash is estimated in the usual way by molybdate. By means of the equation $0.0225 \times 5 \times 86.95 + 13.16a = x(5 \times 86.95 + 12.375a)$, in which x is the amount of phosphoric acid found, there can then be calculated the number of eggs (a) which have been added to 1 lb. (500 grams) of flour, whilst if the yolks alone have been used, the equation becomes $0.0225 \times 5 \times 86.95 + 13.16a_1 = x(5 \times 86.95 + 7.835a_1)$.

To decide whether entire eggs or the yolks only have been used, a more complete analysis, including at least moisture, ash, total phosphoric acid, and nitrogen, must be made. Except in cases where yolk of eggs preserved by adding common salt has been employed, the ash will generally be in larger proportion to the total dry substance where whole eggs have been used than where only the yolks are present; whilst in the latter case phosphoric acid will form a far larger proportion of the total ash than in the former. It is to be observed that, unless an alkali is added, a loss of phosphoric acid will occur when incinerating yolk of egg; with whole eggs, this loss does not take place. For equal percentages of lecithin-phosphoric acid, the nitrogen will be higher when whole eggs are added than when the yolks only have been employed.

M. J. S.

Examination of Commercial Pastry. By SIGISMUND BEIN (*Zeit. Unters. Nahr.-Genussm.*, 1900, 3, 167—168); and by ADOLF JUCKENACK, *ibid.*, 168).—A question of priority.

M. J. S.

General and Physical Chemistry.

Refraction of Normal Salt Solutions. By CARL BENDER (*Ann. Physik.*, 1900, 2, 186—196. Compare Abstr., 1899, ii, 621).—The previous investigations are extended to solutions of potassium chloride at concentrations $N/2$, N , and $2N$, and at temperatures ranging from 10° to 70° , interpolation formulæ being given for each solution for the ranges 10° to 40° and 40° to 70° . With a fair degree of accuracy, that is, ± 2 in the fourth place of decimals, one formula only serves for the three solutions and for pure water for the range 10° to 40° , and one for 40° to 70° , the first term alone differing for the different compounds and for different wave-lengths of light, that is, the dispersion is approximately independent of temperature or concentration, and another formula is given also of the form $A + B\mu + C\mu^2$, where μ is the concentration. The molecular refraction is also calculated by both Gladstone's and Lorenz's formulæ, and the atomic refraction of the potassium is hence obtained, the values 8.5—9.6 (Gladstone) and 5.55—5.78 (Lorenz) being found. L. M. J.

Refractive Power of Methyl Acetate near the Critical Point. By PRINCE BORIS B. GALITZIN and J. WILIP (*Chem. Centr.*, 1900, i, 901; from *Bull. Acad. St. Pétersb.*, [v], 11, 117—196).—In order to determine whether the refractive power of a substance at a temperature near the critical point is the same in the gaseous as in the liquid state, direct measurements of the refractive index were made by the lens and by the prism method. In the first method, the tube containing the liquid served as a cylindrical lens, and in the second a very acute angled prism was inserted in the tube so that one face was parallel to the wall. By the former method, which proved the better, the critical temperature of ethyl acetate was found to be 193.7 — 193.8° . For accurate determinations, a good thermostat is required, and it is necessary to stir the contents of the tube in order to insure thorough mixing of the layers, for even at a temperature above the critical, the density may vary in different parts of the tube, although the temperature and pressure are the same throughout. In one case, it was found that the variations of density amounted to 35 per cent. at the critical point, and to 14 per cent. at 5° above this point. These variations probably indicate that, owing to retardation of ebullition, the substance may exist as a liquid, even above the critical point. When the liquid is thoroughly agitated, the refractive index for the same phase is the same at all parts, and is independent of the total volume occupied by the substance, if the substance is in presence of saturated vapour. If the tube is filled with a homogeneous substance, the refractive index depends only on the total volume, and is independent of the temperature. The relation between the refractive index and the volume for large variations of temperature, and for both the liquid and gaseous states, is well expressed by Lorentz's formula, $C = (x_2 - 1)/(x_2 - 2) \cdot v = 0.3025$.

If the substance is not stirred, it may be assumed that at a tempe-

rature a few degrees below the critical, the refractive index in each layer is the same at the same phase, but as the temperature approaches the critical, the refractive indices of the lower layers tend to become greater. Above the critical temperature, the mean value of the refractive indices of the various layers is that corresponding with the total volume of substance.

E. W. W.

Conditions Determining the Stability of Rotatory Power. By JOSEPH A. LE BEL (*Compt. rend.*, 1900, 130, 1552—1555).—The existence of optical rotation in a chemical compound depends, not only on the asymmetric disposition of at least four dissimilar radicles around a central atom, but also on the stability of the geometric system; the mobility of the substituent radicles produces a loss of optical activity by racemisation.

The stability of an asymmetric system increases with (1) the chemical activity of the central element, (2) the specific volume of the substituent radicles.

The chemical activity of carbon is greater than that of nitrogen, and hence the compounds containing the former element in an asymmetric condition are sufficiently stable to exhibit optical activity at the ordinary temperature; this, however, is not always the case with asymmetric nitrogen. Even with asymmetric carbon compounds containing small radicles, the activity readily disappears; the optical rotation of amyl alcohol is diminished by converting it into its sodium derivative at the ordinary temperature; its rotation greatly decreases on heating it at 100° or 150°, and at 200° it is completely racemised.

The failure to obtain active forms of the salt NHMeEtPrCl is very probably due to the mobility of its light radicles; the compound $\text{C}_{10}\text{H}_{24}\text{NCl}$, obtained by adding methyl to each of these radicles, exhibits optical isomerism, the rotation diminishing as the temperature rises. The salts of the C_{10} bases are, however, less stable than those employed by Pope and Peachey, which contain 17 carbon atoms (*Trans.*, 1899, 75, 1127).

The stability of active substances also depends on the chemical influence exerted by the substituent radicles on one another; it is therefore considerably modified by the replacement of one radicle by another of a different chemical nature: for example, the bromosuccinic acid, obtained by replacing hydroxyl by bromine in malic acid, racemises at the ordinary temperature.

These results indicate that at 100° the presence of four dissimilar radicles attached to a carbon atom is not in itself sufficient to determine the existence of optical rotation, for at this temperature sodium amyloxide and bromosuccinic acid resemble the compounds of active nitrogen, and readily undergo racemisation.

G. T. M.

Solidification and Transition Phenomena of Optical Antipodes. By J. H. ADRIANI (*Zeit. physikal. Chem.*, 1900, 33, 453—476).—The distinction between racemic and pseudoracemic compounds is not as simple as many observers consider; contrary to the opinion of Kipping and Pope (*Trans.*, 1897, 71, 989), the crystallographic form of a racemic compound may be very similar to that of the active components, whilst further, a pseudoracemic compound may be different

in crystallographic form, density, &c. The author considers that there is no satisfactory proof of the existence of a racemic compound in the liquid state as change of volume and production of heat which have been taken as indication of the formation of a racemate also occur when no chemical action takes place; similar doubts also apply regarding the gaseous state. The most satisfactory test for a racemic compound is the complete examination of the melting point curve for mixtures of the two antipodes, and these curves are given for dimethyl tartrate, dimethyl diacetyltartrate, mandelic acid, benzoyltetrahydroquinaldine, camphoroxime, and carvoxime. The first four curves, each consisting of three portions with a central maximum, are typical of the formation of racemic compounds as described by Roozeboom; the fifth is a straight line, and the sixth a continuous curve with a maximum. The last two curves hence indicate a series of mixed crystals, but in the last case no statement can be made regarding the existence of a racemic compound. The transition temperatures were also determined for the whole series of the camphoroxime mixtures, and it was found that the continuous series of the β -modification changes into a continuous series of the α -modification, the transition curve being continuous with a central minimum. Although only mixed crystals may exist at the melting point, yet it is possible that racemic compounds may exist at the ordinary temperature, and it is shown that this is probably the case with carvoxime (compare Roozeboom, this vol., ii, 64, 70, 132).

L. M. J.

Asymmetry and Vitalism. By C. ULPANI and S. CONDELLI (*Gazzetta*, 1900, 30, i, 344—382).—A discussion of Japp's Sectional Address at the British Association in 1898 and of the controversy to which it gave rise. The views of Pasteur, Peré, Hahn, and Fischer are also discussed. The authors find that whilst *Penicillium glaucum* destroys *l*-lactic acid, *d*-alanine, and *d*-tartaric acid, the cholera bacillus attacks *d*-lactic acid, *l*-alanine, and *d*-tartaric acid; these results throw doubt on Japp's biological theory of the propagation of life in an asymmetric sense.

T. H. P.

The Lead Accumulator. By MARTIN MUGDAN (*Zeit. Elektrochem.*, 1899, 6, 309).—The author shows that, when an accumulator is discharged, lead sulphate separates on both the positive and negative plates in almost theoretical quantity, and that no lead oxide is formed. If sodium sulphate is used as the electrolyte in place of sulphuric acid, however, some lead oxide is formed on the positive plate. A partially oxidised negative plate takes up sulphuric acid very slowly, whereas a positive plate containing oxide absorbs the acid very rapidly. The potential difference between a negative (spongy lead) plate and sulphuric acid of given concentration is independent of the quantity of lead sulphate on the plate. The alterations in the E.M.F. of an accumulator during charge and discharge are due to local changes of the concentration of the acid at the electrodes. When at rest, the condition of affairs may be represented thus: $\text{Pb, PbSO}_4 \mid \text{acid} \mid \text{PbSO}_4, \text{PbO}_2$. During charge, the acids at the electrodes are more, but during discharge, are less concentrated than the main bulk of the acid. The total E.M.F. is therefore obtained by

superimposing the E.M.F.'s of two concentration cells on the main E.M.F. The two concentration cells may be represented thus: $\text{Pb, PbSO}_4 \mid \text{dil. or conc. acid} \mid \text{acid} \mid \text{PbSO}_4, \text{Pb}$ and $\text{PbO}_2, \text{PbSO}_4 \mid \text{dil. or conc. acid} \mid \text{normal acid} \mid \text{PbSO}_4, \text{Pb}$. The E.M.F.'s of these concentration cells are calculated from Nernst's theory (see Dolezalek, this vol., ii, 2), and compared with actual measurements made by the author. For acids containing less than 0.75 gram-mol. per litre, the agreement is excellent. A change of concentration at the lead dioxide plate makes about 1.4 times as much difference in the E.M.F. as an equal change at the lead plate. Further, the concentration of the acid at the lead dioxide plate increases or decreases during charge and discharge $1 + \frac{2v}{u}$ times as quickly as that at the lead plate (u and v are the relative mobilities of the H and SO_4 ions). The effect of the changes of concentration at both electrodes is to diminish the E.M.F. of the cell during discharge and increase it during charge.

T. E.

Chemical Equilibrium and Electromotive Force. By H. DANNEEL (*Zeit. Elektrochem.*, 1899, 6, 293).—From theoretical considerations, the author draws the conclusion that, when a metal is precipitated from a solution of one of its salts by another metal, the ratio of the concentrations of the ions of the two metals in the solution when equilibrium is attained is the same as the ratio of the solution tensions of the two metals. This conclusion is tested experimentally in the case of the precipitation of silver from a solution of silver iodide in hydriodic acid by hydrogen. The concentration of the hydrogen ions when equilibrium is attained is calculated to be 0.057 gram-mol. per litre at 18° , whilst the concentration 0.042 at 13° is found experimentally. The further conclusion is drawn that, in reactions of this kind, the final equilibrium is independent of the nature of the anion.

T. E.

Additivity of Atomic Heats. By STEFAN MEYER (*Ann. Physik.*, 1900, 2, 135—140).—By the comparison of the molecular heats and molecular volumes of a large number of compounds with the sum of the atomic heats or atomic volumes of the components, it is seen that the molecular heat is only equal, or approximately equal, to the sum of the atomic heats in those cases where the molecular volume is also equal or approximately equal to the sum of the atomic volumes, and the differences in the two cases are, moreover, in the same sense.

L. M. J.

Boiling Point Curves. By CLARENCE L. SPEYERS (*Amer. Jour. Sci.*, 1900, 9, 341—344).—The expression $n_1/(n_2 + n_1) = (p - p')/p$, previously used by the author for the determination of molecular weights in liquid mixtures (Abstr., 1899, ii, 145), may also be used to calculate the boiling point curves of the latter if the states of molecular aggregation of the components are known. The curves so calculated agree well with the experimental determinations in the case of mixtures of carbon tetrachloride with benzene or chloroform; for benzene and chloroform, however, the agreement is not so good, but fair accord was obtained for mixtures of benzene and ethyl

alcohol, where complex molecules are known to occur. If the molecular weights of the components are normal, the curves will be straight lines if $dp_1/dt_1 = dp_2/dt_2$, while if $dp_2/dt_2 > dp_1/dt_1$, the curve will be convex or concave to the axis of abscissæ according as $p_2 >$ or $< p_1$. A mixture cannot have a minimum boiling point unless one or both components have abnormal molecular weights. In the first case, a minimum would probably occur when the constituent with the lower vapour pressure is associated; in the latter case, absence of a minimum would be exceptional, although possible. L. M. J.

Phenomenon Noticed in the Cooling of Superfused Substances. By R. MORESCHINI (*Gazzetta*, 1900, 30, i, 339—344).—Mixtures of fatty acids obtained from soap exhibit the phenomenon of superfusion, the temperature at which resolidification occurs varying with the method of determination employed. When such a mixture is heated in a tube to, say, 15° above its melting point, and then allowed to cool in a constant temperature air-bath, conveniently 15° below the melting point, the rate of cooling diminishes regularly until the melting point is reached, when a sudden diminution takes place; cooling afterwards proceeds regularly, although more slowly than before. In the case of pure substances, however, this sudden change in the rate of cooling occurs just at the melting point, whilst with mixtures of fatty acids, especially if much oleic acid is present, it appears at a temperature about 0.15° above the melting point.

T. H. P.

Determination of the Transition Temperature of Monotropic Dimorphous Substances. By RUDOLF SCHENCK (*Zeit. physikal. Chem.*, 1900, 33, 445—452).—In the case of a monotropic dimorphous substance, the transition temperature lies above the melting point, and hence cannot be directly determined. If the melting points of the two modifications be lowered by the addition of a foreign substance, the depression will be less for the stable form, in consequence of the smaller value of the latent heat of fusion—if curves be drawn for melting point against concentration of foreign substance, the curves, by extrapolation, will meet at a certain negative concentration and higher temperature. For this concentration, there is no physical interpretation, but the author considers the temperature to be the transition temperature of the compounds. By this means, the transition point of *m*-nitro-*p*-acetyl-toluidine was found to be 105.9° , the melting points of the two modifications being 93.32° and 91.58° . For monochloroacetic acid, the melting points of the two varieties of which were found to be 56.3° and 61.5° , no result could be obtained, owing to the very slight difference between the depression constants.

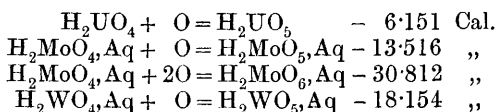
L. M. J.

Apparatus for Determining the Calorific Value of Fuels. By GAETANO MAGNANINI and V. ZUNINO (*Gazzetta*, 1900, 30, i, 395—401).—A modified form of Lewis Thompson's calorific bomb is described, the use of an oxidising mixture to burn the fuel being obviated, and the combustion carried on in a regular stream of oxygen. A series of 15 different samples of coal were examined in the new

apparatus and good results obtained, the calorific values found being in every case but two higher than the numbers yielded by the Lewis Thompson method.

T. H. P.

Thermochemistry of Hyperacids. By L. PISSARJEWSKY (*J. Russ. Phys. Chem. Soc.*, 1900, 32, 155—169).—The following heats of neutralisation by sodium hydroxide of acids of the elements of the sixth series in Mendeléeff's table have been determined: Pyrouranic acid, $\text{H}_2\text{U}_2\text{O}_7$, +17.559 Cal.; tungstic acid, H_2WO_4 , +13.698 Cal.; permolybdic acid, H_2MoO_5 , +13.248 Cal.; molybdic acid, H_2MoO_4 , +21.278 Cal. Comparing the heats of neutralisation of molybdic and tungstic acids with the value, +24.720 Cal., for chromic acid, it is seen that as the atomic weight of the element of this series increases, the acid function of the corresponding acid decreases. The following heats of reaction were also determined:



T. H. P.

Absorption. VI. Absorption of Matters from Solution. By JACOBUS M. VAN BEMMELEN (*Zeit. anorg. Chem.*, 1900, 23, 321—372).—In the partition of a crystalloid between a colloid or porous substance and the liquid solution, the ratio of the concentrations may be greater than, equal to, or less than, unity; the last case, termed by the author negative absorption, has been observed when kaolin is added to a solution of salt, the concentration of the latter in the solution being thereby increased. The absorption of the crystalloid is influenced by various factors. (1) By the structure and state of the colloid; thus, red colloidal manganese peroxide absorbs more acid or salt from an aqueous solution than does the black, and the absorptive power of stannic or metastannic acid is dependent on its condition. (2) By the nature of the solvent, picric acid is absorbed by silk in greater quantity from an aqueous solution than from an alcoholic solution, and not at all from a benzene solution; this is not merely due to the solubility in the different solvents, as picric acid is more soluble in alcohol than in either of the other two. (3) By the nature of the solute; the metastannic acid hydrogel, for example, absorbs potassium chloride but slightly, but hydrogen chloride very strongly. (4) By the molecular state of the solute in the solutions, and (5), by the temperature. The case of the absorption of two compounds from a solution by a colloid is greatly complicated by the influence of each on the absorption of the other, and of the compounds produced by their interaction. In the colloid, hydrolysis frequently occurs even in the case of salts of strong acids or bases, as, for instance, potassium sulphate or chloride, from solutions of which various hydrogels absorb an excess of base (compare this vol., ii, 338; Abstr., 1899, ii, 12, 84, 487).

L. M. J.

Theory of Capillarity. By G. BAKKER (*Zeit. physikal. Chem.*, 1900, 33, 477—499).—The author considers the usual treatment and

derivation of the laws of capillarity to be unsatisfactory, and gives a different method for their derivation, but without deducing any important new results.
L. M. J.

Solution Tension of Zinc in Ethyl Alcohol. By HARRY C. JONES and ARTHUR W. SMITH (*Amer. Chem. J.*, 1900, 23, 397—403).—Jones's experiments (Abstr., 1894, ii, 374) have shown that the solution tension of silver is considerably less in alcoholic than in an aqueous solution of its salts. As the solution tension of silver is very small, the authors have extended the investigations to zinc, the solution tension of which is very great. The dissociation of a $N/10$ solution of zinc chloride in ethyl alcohol was found by the boiling point method to be 6.5 (this vol., ii, 187); Kahlenberg had found the E.M.F. of the chain zinc | aqueous $N/10$ zinc chloride | alcoholic $N/10$ zinc chloride zinc to be 0.19 volt, from which the value 1.9×10^{10} atmos. is obtained for the solution tension of the zinc in alcohol. By the determination of the E.M.F. of the alcoholic electrode alone (0.327 volt), the value 2.7×10^{-10} atmos. is obtained for the solution tension, agreeing fairly with the previous value, and about 10^{-8} times the solution tension in water, so that metals cannot be regarded as possessing a definite solution tension independent of the solvent.
L. M. J.

Changes of Solubility by Addition of Salts. By VICTOR ROTHMUND (*Zeit. physikal. Chem.*, 1900, 33, 401—414).—Although it is frequently assumed that the addition of a salt should have no effect on the solubility of a non-electrolyte in water, yet Gordon (Abstr., 1896, ii, 154) and Roth (Abstr., 1898, ii, 18) have shown that the solubility of gases in water is diminished by the addition of salts, and Euler has shown that the solubility of ethyl acetate is similarly decreased (this vol., ii, 196), and to about the same extent, the relative order of the salts examined being also similar in the various cases. The author has determined the influence of the addition of salts on the solubility of phenylthiocarbamide, and curves are given for salt concentration against solubility, these curves being approximately straight lines. The sulphates and carbonates produce the greatest depression, the equivalent solubility depression being about 0.4; nitrates were found to have the least effect, ammonium nitrate causing an increase of solubility, whilst the order of the salts is also the same as that found for carbon dioxide, hydrogen, nitrous oxide, and ethyl acetate. The equivalent solubility depression $1/n.(s_0 - s)/s_0$ was found to be independent of temperature, hence s/s_0 is constant, so that $d \log s / dT = d \log s_0 / dT = q/2T^2 = q_0/2T^2$, where q is the heat of solution, which is hence the same in salt solutions as in pure water.
L. M. J.

Chemical Kinetics and Free Energy of the Reaction
 $2\text{HI} + 2\text{Ag} \rightleftharpoons 2\text{AgI} + \text{H}_2$. By H. DANNEEL (*Zeit. physikal. Chem.*, 1900, 33, 415—444).—The E.M.F. of a cell consisting of silver and hydrogen electrodes in normal solutions of the corresponding ions is 0.78 volt, and hence it follows that the E.M.F. of any similar cell is $0.78 + 0.058 \log C_{\text{Ag}}/C_{\text{H}}$ volts where C_{Ag} and C_{H} are the concentrations of the silver and hydrogen ions. The solubility of silver iodide is

not known with certainty, but accepting the value 10^{-8} , it follows that at the concentration $C_H = 0.053$ the E.M.F. of the cell is zero, and equilibrium obtains. The equilibrium concentration obtained by direct experiment was 0.043, a value which gives $0.567 + 10^{-8}$ as the solubility of silver iodide, a value lower than those previously obtained by other methods. The reaction-velocities in each direction were determined; the values indicate that the reaction proceeds as $\text{Ag} + \text{HI} \rightleftharpoons \text{AgI} + \text{H}$, so that the hydrogen takes part in the reaction as H, not as H_2 . The equilibrium constant calculated from the reaction velocities is in complete accord with the direct determination. The value of the E.M.F. of any similar cell is $0.1154 \log C/C_0$, where C is the actual and C_0 the equilibrium concentration of the hydrogen, but the values experimentally obtained are not in accord with those so calculated, an almost constant difference of 0.02 volt being found. No explanation could be given, although it is pointed out that a higher pressure of hydrogen in the electrode would cause such a difference.

L. M. J.

Reactions in Water and Acetone. By PAUL ROHLAND (*Chem. Zeit.*, 1900, 24, 312—314).—Owing to differences in the extent of the dissociation and in solubility, many reactions proceed differently in aqueous and acetone solutions. The colour of dilute solutions of copper salts is alike in both solvents, but with moderately strong solutions the colour differs, owing to the smaller value of the dissociation in acetone. The velocity of an ionic reaction may also be very small; thus silver nitrate and sodium dichromate gave no precipitate until the lapse of 30 seconds or more, whilst the precipitates frequently differ from those obtained in aqueous solutions, being probably allotropic forms. Anomalous reactions as those previously recorded (*Abstr.*, 1899, ii, 144) may occur, and fresh examples are given. Many reactions dependent on particular ions, as, for example, the action of hydroxyl compounds on the halogens, and on various indicators, may not occur in acetone solutions, owing to the absence of the particular ion involved.

L. M. J.

Behaviour of Perfumes with Liquid Air. By HUGO ERDMANN (*J. pr. Chem.*, 1900, [ii], 61, 225—228).—Preliminary experiments show that some perfumes lose their odour more or less completely when dissolved in liquid air, but on shaking the flask the odour is strongly apparent. The perfumes dissolved in liquid air therefore evaporate with it; hence it is possible that the volatility of any perfume does not depend alone on its vapour tension, but also on its specific solubility in air.

R. H. P.

Apparatus for Sublimation. By C. N. RIIBER (*Ber.*, 1900, 33, 1655—1657).—The author describes an apparatus for subliming substances under reduced pressure. For heating the apparatus, a Lothar Meyer air-bath, or simply two iron dishes fitting into one another, but separated by a layer of air and covered with an asbestos lid, may be employed. The apparatus itself consists of a horizontal glass cylinder ground into a glass cup, in which the substance to be sublimed is placed, the upper end of the cylinder is drawn out into

a narrow tube, which can be attached to the pump. The process of sublimation is quickened if the cup and cylinder do not fit quite airtight, as a gentle current of warm air is thus kept passing over the substance. The apparatus may also be employed for separating two substances of different volatility, for the estimation of water of crystallisation, &c.

J. J. S.

Lecture Experiments Illustrating Equilibrium and Dissociation. By JULIUS STIEGLITZ (*Amer. Chem. J.*, 1900, 23, 404—408).—The effect of excess of one of the products on the dissociation of a compound is easily seen by heating two tubes containing bromine with (1) an equivalent quantity, and (2) an excess of phosphorus tribromide. It is still more marked if phosphorus bromodichloride be used, and the difference between this and the previous case forms an illustration of the different magnitudes of dissociation constants. The decrease of electrolytic dissociation, on addition of one of the ions, is well seen on adding an ammonium salt to a solution of phenolphthalein coloured red by a few drops of a dilute ammonia solution, the red colour almost disappearing in consequence of the decrease of concentration of the hydroxyl ions. A somewhat similar result is obtained by the addition of an acetate to a solution of methyl-orange reddened by a drop of acetic acid.

L. M. J.

Inorganic Chemistry.

Limits of Combustibility of Hydrogen and Gaseous Hydrocarbons when Diluted with Large Volumes of Air and Passed over Red Hot Cupric Oxide. By ARMAND GAUTIER (*Compt. rend.*, 1900, 130, 1353—1360).—Definite mixtures of hydrogen or methane or both with air previously freed from hydrogen and carbon compounds, were passed slowly through two consecutive tubes containing cupric oxide heated just to redness. With two tubes each 35 cm. long, hydrogen is completely oxidised even when diluted with 5000 times its volume of air, but it is noteworthy that only 70 per cent. of the oxidation takes place in the first tube.

Methane, however, under similar conditions, is incompletely burnt. With two tubes each 30 cm. long and a dilution of 1 in 4000, 71.6 per cent. of hydrogen and 58.9 per cent. of the carbon are burnt; with a dilution of 7 in 100,000, 45.2 per cent. of hydrogen and 36 per cent. of carbon. With methane, 16 parts, and hydrogen, 8 parts, in air, 100,000 parts, all the free hydrogen, 58.3 per cent. of the hydrogen in the methane, and 47.4 per cent. of the carbon in the methane are burnt. It would seem, therefore, that the presence of free hydrogen promotes the oxidation of the hydrogen of the methane. The use of a third tube of cupric oxide, even 80 cm. long, has no appreciable influence on the results obtained with mixtures of hydrogen and hydrocarbons.

C. H. B.

Higher Hydrogen Peroxides. By A. BACH (*Ber.*, 1900, 33, 1506—1517).—Whilst hydrogen dioxide, H_2O_2 , when reduced with potassium permanganate, gives 5O_2 for each 2KMnO_4 , hydrogen tetroxide, H_2O_4 , should give 10O_2 for each 2KMnO_4 . The method adopted in order to detect the presence of higher hydrogen peroxides consisted in measuring the volume of gas liberated in the titration with potassium permanganate and comparing it with that calculated from the ratio $2\text{KMnO}_4 : 5\text{H}_2\text{O}_2$. The proportion of gas found in titrating hydrogen peroxide from different sources was as follows :

From barium peroxide.....	1
„ oxidation of palladium hydride.....	1.07
„ sodium dioxide	1.17
„ potassium tetroxide	1.28
„ a mixture of hydrogen peroxide with two volumes of concentrated sulphuric acid...	1.65

From these results, the existence of a higher hydrogen peroxide is assumed, and the formula H_2O_4 is assigned to it from analogy to K_2O_4 , and also because H_2O_3 is regarded as a substance which would probably have no oxidising power.

T. M. L.

[The large volume of oxygen produced from a mixture of hydrogen peroxide and sulphuric acid is readily explained by the presence of a 'persulphuric acid' in the mixture; this was demonstrated by Berthelot as long ago as 1878, and it was found that, whilst it does not reduce potassium permanganate, it is readily hydrolysed to sulphuric acid and oxygen.—T. M. L.]

Evolution of Chlorine by the Aid of Manganese Dioxide. By LEONHARD WACKER (*Chem. Zeit.*, 1900, 24, 285).—Manganese dioxide or one of its hydrates is obtained when chlorine gas is passed into a solution of crystallised manganese chloride in concentrated hydrochloric acid for some hours, and the dark coloured liquid thus obtained poured into warm water. The author thinks that this confirms the conclusion that manganese tetrachloride is the first product formed by the action of hydrochloric acid on manganese dioxide (compare Meyer and Best, this vol., ii, 77).

J. J. S.

Electrolytic Preparation of Hypochlorites. By ADOLF SIEVERTS (*Zeit. Elektrochem.*, 1900, 6, 364, 374).—The experiments were made in order to decide whether the yield of hypochlorite in the electrolysis of solutions of the chlorides of the alkali or alkaline earth metals is increased by an increased current density. Oettel had observed an increased yield with the electrolyte at rest, and Schoop a decreased yield with a flowing electrolyte. In the author's experiments, the solution flows at constant speed through the cell, the quantity of hypochlorite formed after the passage of a definite quantity of electricity at varying current density being determined. An increased yield was observed at higher current densities both with sodium and potassium chlorides. The yield of hypochlorite is very good at the beginning of an experiment, when its concentration in the solution is small, but it decreases rapidly (owing to cathodic reduction) as the concentration rises.

Further experiments were made in order to decide whether the superior bleaching properties of electrolytic hypochlorite solutions are due to the presence of free hypochlorous acid. The free hypochlorous acid present is determined by a method due to Jorre, depending on the reactions $\text{MOCl} + \text{H}_2\text{O}_2 = \text{MCl} + \text{H}_2\text{O} + \text{O}_2$ and $\text{HOCl} + \text{H}_2\text{O}_2 = \text{HCl} + \text{H}_2\text{O} + \text{O}_2$. The hydrogen chloride liberated is finally titrated. The following table contains the principal results. The solutions were all treated in the same way and the time which they required to bleach a piece of turkey red cloth noted.

	Grams salt per 100 c.c.	Hypochlorite current efficiency.	Per cent. of HOCl free.	Time of bleaching.	Per cent. of hypochlorite undecomposed after 24 hours.
10 grams	NaCl.....	51.7	0	5½ hours	98
12.7 „	KCl	44.4	0	4 „	98
9.5 „	CaCl ₂ ...	73.4	49.3	15 min.	45
3.48 „	MgCl ₂ }	62.1	94.9	10 „	90
+ 8 „	NaCl }				

The effect of the presence of free hypochlorous acid is quite clear. A solution of pure magnesium chloride gave a liquid which readily decomposed, contained free chlorine, and was not further investigated.
T. E.

Electrolytic Formation of Chlorates. By HEINRICH WOHLWILL (*Zeit. Elektrochem.*, 1900, 6, 410).—A continuation of the discussion with Forster (see Abstr., 1899, 278; this vol., ii, 72, 400). T. E.

Chlorine Heptoxide. By ARTHUR MICHAEL and WALLACE T. CONN (*Amer. Chem. J.*, 1900, 23, 444—446).—The method described by Roscoe (*Trans.*, 1863, 16, 82) for the preparation of perchloric acid is improved by heating the perchlorate and sulphuric acid under 10—20 mm. pressure. Perchloric acid boils at 19° under 11 mm. pressure. When it is mixed with alcohol or ether, no explosion occurs; it dissolves in benzene, forming a green solution which gradually becomes charred. Iodine dissolves in the acid with the production of a dark solution which, on exposure to bright light, becomes converted into a white solid; when this white substance is heated, it is decomposed into iodine and iodic acid (compare Vorländer and Schilling, this vol., ii, 340).

Chlorine heptoxide is obtained by slowly adding perchloric acid to phosphoric oxide cooled below -10° ; the mixture is left for a day and then gradually warmed until the new oxide distils over. It is a colourless, very volatile oil, which boils constantly at 82° under ordinary pressure; on standing for 2—3 days, it becomes greenish-yellow and evolves a greenish gas. It explodes violently on percussion or when brought into a flame, but is without action on wood or paper. By the action of water on the oxide, it is gradually converted into perchloric acid. It dissolves in dry, well-cooled benzene and slowly attacks it. It reacts with iodine with liberation of chlorine and formation of a white substance which is probably iodine heptoxide; this decomposes at 380° with the production of iodine and oxygen. Chlorine heptoxide is not, however, similarly attacked by bromine.
E. G.

Preparation, Properties, and Analysis of Thionyl Fluoride. By HENRI MOISSAN and PAUL LEBEAU (*Compt. rend.*, 1900, 130, 1436—1442. Compare this vol., ii, 341).—Thionyl fluoride, which was first obtained by Meslans (*Bull. Soc. Chim.*, 1896, [iii], 15, 391), is most conveniently prepared by mixing together arsenic trifluoride (2 mols.) and thionyl chloride (3 mols.) and heating the mixture at 100° ; it is separated from arsenic trichloride and traces of its generators by fractional distillation at low temperatures. It is also produced by the action of fluorine on thionyl chloride; this reaction, however, is somewhat complicated, and the thionyl fluoride is contaminated with chlorine and a more volatile sulphur oxyfluoride which is not absorbed by water.

Thionyl fluoride is a colourless gas which boils at -32° , fumes slightly in moist air, and has a suffocating odour; it has no action on mercury at the ordinary temperature. Its composition was determined both by synthesis from weighed quantities of its generators and also by volumetric and gravimetric analyses. The volumetric determination was made by heating the gas in a dry glass vessel at 400° ; under these conditions, 4 vols. of the gas yield 6 vols. of gaseous products in accordance with the following equation, $2\text{SOF}_2 + \text{SiO}_2 = \text{SiF}_4 + 2\text{SO}_2$. Its decomposition by water ($\text{SOF}_2 + \text{H}_2\text{O} = \text{SO}_2 + \text{H}_2\text{F}_2$) furnishes a method for the gravimetric analysis, the sulphurous acid being estimated iodometrically and the fluorine by precipitation as calcium fluoride. The gas is soluble in arsenic trichloride, ether, turpentine, or benzene, and is absorbed by fused sodium or tin; when treated with hydrogen chloride over mercury, a gaseous mixture is produced which gradually attacks this metal.

The action of the electric discharge from an induction coil on thionyl fluoride contained in glass vessels is similar to that of heat; when this decomposition takes place in the presence of hydrogen, the sulphur dioxide produced undergoes reduction, and hydrogen sulphide, sulphur, and water are produced; the last named reacts with the silicon fluoride, giving rise to a small quantity of hydrofluosilicic acid.

The presence of oxygen does not affect the decomposition of the thionyl compound as produced by the action of heat, but when a mixture of the two gases is submitted to the action of the induction spark a certain amount of the more volatile sulphur oxyfluoride is produced. Sulphur and phosphorus do not act on the gas at 500° ; water, hydrogen fluoride, and sulphur are produced by the action of hydrogen sulphide at high temperatures; there is, however, no interaction in the cold.

Ammonia is absorbed by thionyl fluoride, yielding first an orange compound having the composition $2\text{SOF}_2 \cdot 5\text{NH}_3$, and finally a white substance corresponding with the fixation of 7NH_3 by 2SOF_2 ; when treated with hydrogen chloride, the latter product is decomposed, giving rise to sulphur dioxide and sulphur. G. T. M.

Estimation of Sulphuric Acid in the Presence of Iron: Solid Solution and the Hydrolysis of Chromium and Iron Salts. By THEODORE W. RICHARDS (*Zeit. anorg. Chem.*, 1900, 23, 383—390).—The paper contains a theoretical criticism of Kuster

and Thiel's work on the estimation of sulphuric acid in the presence of iron (Abstr., 1899, ii, 247, 611; this vol., ii, 242). Since a precipitate of calcium carbonate obtained in a solution saturated with salt contains only 0.1 per cent. of sodium chloride, it is evident that the precipitation of impurities together with barium sulphate which amount to several per cent. is a different phenomenon. This the author calls *occlusion* to distinguish it from mechanical inclusion, and compares it with the occlusion of hydrogen by palladium. Aluminium sulphate and green chromium sulphate are also occluded by barium sulphate. The occlusion is probably brought about by the formation of an electrically neutral substance or complex. The nature of the groups which cause the occlusion in the case of iron, chromium, and aluminium salts is not determined, but they are probably of a basic character and similar to the basic complex described by Recoura (Abstr., 1896, ii, 27) and Whitney (Abstr., 1896, ii, 525). The green chromium sulphate solution probably contains not only a basic complex, but also a chromosulphuric acid which is not precipitated by barium solutions and is only slightly occluded by barium sulphate as it is strongly dissociated.

E. C. R.

Spontaneous Decomposition of Thiosulphuric Acid. By ARNOLD F. HOLLEMAN (*Zeit. physikal. Chem.*, 1900, 33, 500—501. Compare van Oettingen, this vol., ii, 400).—The author had previously shown that opalescence must not be regarded as the first indication of the decomposition of thiosulphuric acid, for if the solution is neutralised before opalescence is produced, it still occurs later. The decomposition is also not necessarily entirely due to hydrogen and S_2O_3 ions, as there is no evidence against the view that the undissociated molecules are also reactive.

L. M. J.

Tellurium. By F. D. CRANE (*Amer. Chem. J.*, 1900, 23, 408—425).—Tellurium may be obtained from the dross produced in the final purification of the precious metals from the electrical refining of copper (compare Whitehead, Abstr., 1896, ii, 164) by extracting it with hydrochloric acid and precipitating by means of sodium hydrogen sulphite. In order to remove selenium, the precipitate is allowed to act as the positive pole of an electrolytic cell containing hydrochloric acid; the nascent chlorine effects the solution of the tellurium, the selenium remaining undissolved. Further purification is carried out by boiling the precipitated tellurium with a reserve portion of the solution from which it has been obtained, in order that any metallic elements with which it may be contaminated may be dissolved and an equivalent quantity of tellurium precipitated.

Keller (Abstr., 1898, ii, 638) has stated that selenium and tellurium may be separated by means of ferrous sulphate, the selenium being precipitated, whilst the whole of the tellurium remains in solution. The author finds that this is only true if the tellurium is present entirely as tetrachloride, for if the solution contains any dichloride, some tellurium is always precipitated. When tellurium is added in excess to a mixture of selenium dichloride and tellurium tetrachloride

dissolved in hydrochloric acid, the selenium becomes completely replaced by tellurium, and is thus removed from the solution.

Tellurium tetrachloride dissolves in water, forming a yellow solution; when this solution is diluted, it yields a precipitate of tellurous acid, which gradually changes into the crystalline dioxide. If a metal, such as iron, arsenic, or antimony, is present, the precipitate appears to consist of a double oxychloride. E. G.

Some Properties of Liquid Ammonia. By C. FRENZEL (*Zeit. Elektrochem.*, 1900, 6, 477, 487, and 493).—The author has determined certain properties of very carefully purified liquid ammonia. The specific conductivity of the purest ammonia obtained was 1.33×10^{-7} ohms per cm. at -79° . The conductivity increases 1.9 per cent. of its value at 60° per degree rise of temperature. The conductivity increases and the temperature coefficient decreases with increasing impurity of the ammonia; in these particulars, it resembles water. By observations of the current which passes between a small cathode and a large anode through solutions of salts in ammonia when the applied E.M.F. is gradually increased, it is shown that there are three points at which anions, formed from the ammonia itself, are discharged. The author concludes that electrolytic dissociation of

NH_3 into H^+ , NH_2^- , NH^- , and N^{--} takes place. The addition of traces of water to liquid ammonia produces a comparatively very small increase in its conductivity. This is probably due to the fact that the greater part of the water remains uncombined, a very small portion forming $\text{NH}_4\cdot\text{OH}$. T. E.

Azoimide. By THEODOR CURTIUS and AUGUST DARAPSKY (*J. pr. Chem.*, 1900, [ii], 61, 408—422. Compare Curtius and Rissom, *Abstr.*, 1899, ii, 90).—The precipitation of aluminium hydroxide from a solution of ammonia-alum by sodium azoimide proceeds quantitatively if the azoimide set free is expelled by boiling. Chrome alum gives a green solution of chromium azoimide which is completely hydrolysed on boiling, the whole of the chromium being precipitated as hydroxide; a second *basic chromium azoimide* containing $1\text{Cr}:1\text{N}_3$ has been precipitated as a green salt from the solution by adding alcohol and ether. Ferric alum gives a blood-red solution of the azoimide which soon deposits a brown basic azoimide.

Zirconium and thorium give no azoimide, but are completely precipitated as hydroxides. Yttrium resembles chromium in that it gives a soluble azoimide, from which the hydroxide is precipitated on boiling. Lanthanum, cerium, and didymium give soluble azoimides, from which basic azoimides are precipitated on boiling containing 1La, Ce, or Di to 2N_3 . Uranium gives a much more stable azoimide, which is hydrolysed very slowly to uranyl hydroxide on boiling the solution.

On precipitating with alcohol and ether, manganese azoimide only gives the basic azoimide already obtained by evaporation, but *nickel azoimide*, $\text{NiN}_6 + \text{H}_2\text{O}$, is thrown down as a green, explosive powder, which dissolves again in water to a clear solution.

Arsenic dissolves in azoimide, but the azoimide is completely hydrolysed on evaporating the solution; antimony behaves similarly, but is only dissolved very slowly.

Azoimide is partially reduced to ammonia by zinc, and also by arsenic or antimony, but not by sodium amalgam; no hydrazine, hydroxylamine, or 'triimide' could be detected amongst the products of reduction.

T. M. L.

Preparation of Free Hydroxylamine. By RUDOLF UHLENHUTH (*Annalen*, 1900, 311, 117—120).—Although hydroxylamine oxalate yields the free base on distillation, the method is not suitable for the preparation of the purified substance, because water and carbon dioxide are produced at the same time. When hydroxylamine phosphate is distilled under reduced pressure, a very pure specimen of the base can be obtained; under 13 mm. pressure, distillation occurs at 135—137°, and the distillate solidifies almost immediately when the receiver is plunged into melting ice.

M. O. F.

Formation of Nitric Acid during Combustion: Carbon. By MARCELLIN P. E. BERTHELOT (*Compt. rend.*, 1900, 130, 1345—1353).—In the course of his researches on heats of combustion, the author has determined the quantities of nitric acid formed by the action of water and air on the nitrogen oxides produced during combustion in oxygen containing a small proportion of nitrogen, either at atmospheric pressure or in the calorimetric bomb. When amorphous carbon is burnt in the bomb under a pressure of 25 atmos. in oxygen containing 8 per cent. by volume of nitrogen, about 0.051 gram of nitric acid is formed per gram of carbon, although the actual amount varies with the rate of combustion, &c. The ratio of carbon dioxide to nitrogen is approximately $106\text{CO}_2:\text{HNO}_3$. With graphite, under similar conditions, the quantity of nitric acid formed is only about one-fifth, and with diamond only about one-third of that formed in the case of amorphous carbon.

At the ordinary pressure in the same mixture of nitrogen and oxygen, even less than 1 milligram of nitric acid is formed per gram of amorphous carbon, whilst with air in place of oxygen, the proportion barely reaches 0.1 milligram per gram. Small though this amount is, the total quantity of nitric acid formed during the combustion of such substances as coal, petroleum, &c., must in the aggregate be very large. In the Department of the Seine it will amount to at least 8 kilograms of nitric acid per hectare per annum.

C. H. B.

Formation of Nitric Acid during Combustion: Sulphur, Metals. By MARCELLIN P. E. BERTHELOT (*Compt. rend.*, 1900, 130, 1430—1436. Compare preceding abstract).—When sulphur is burnt in atmospheric air or in oxygen containing 5—8 per cent. of nitrogen, a small amount of the latter element always undergoes oxidation; the results are therefore similar to those obtained in the combustion of carbon, although the amount of nitric acid produced when the action takes place in oxygen is much smaller. When the sulphur is burnt in compressed oxygen containing a small quantity of nitrogen, traces of ammonia can also be detected. The combustion of iron and zinc

under these conditions is not attended by the oxidation of nitrogen. The difference in the electrical properties of the combustibles and their oxides is suggested as the cause of this disparity. These phenomena were investigated quantitatively, and the paper contains a full discussion of the numerical data.

G. T. M.

Supposed Transformation of Phosphorus into Arsenic. By CLEMENS WINKLER (*Ber.*, 1900, 33, 1693—1697).—A destructive criticism of a paper by F. Fittica (*Leopoldina, Halle*, 1900, 36, 3, 40), in which it is stated that phosphorus can be partly transformed into arsenic by treatment with ammonium nitrate at 200°. Fittica's experiments have been repeated, and it is shown that the arsenic he obtained was really derived from impurities in the materials used.

R. H. P.

Dihydroxides. By ROBERT DE FORCRAND (*Compt. rend.*, 1900, 130, 1555—1558).—The addition of 1 mol. of hydrogen peroxide to aqueous solutions containing 2 mols. of sodium, potassium, or lithium hydroxides is attended by a heat disturbance of +5.821, +6.123, and +6.533 Cal. respectively; on adding a second mol. of the peroxide, more heat is developed, the additional amounts being respectively +4.845, +4.510, and +4.826 Cal. When ammonia and methylamine are substituted for these alkalis, the heat change, due to the first mol. of peroxide, is +0.589 and +2.584 Cal. respectively; the second molecule producing a further development of +0.464 and +1.464 Cal.

Appreciable thermal effects attend the addition of a third mol. of the peroxide to solutions of sodium and potassium hydroxides, the increments being +0.809 and +0.491 Cal. respectively; with lithium hydroxide, however, the change is only +0.005 Cal. These results point to the existence of compounds of the types $\text{NaO}\cdot\text{OH}$ and $\text{NaO}\cdot\text{ONa}$ and the heat of neutralisation of the acidic functions of hydrogen peroxide by various basic hydroxides can be calculated from the above data. The values of these constants are intermediate between those of the glycols and dihydric phenols. In the *m*- and *p*-dihydroxybenzenes, the heats of neutralisation of the first and second hydroxyl groups are approximately equal; the numerical values of these constants differ widely in the case of catechol and hydrogen peroxide which contain these radicles in close proximity to each other; the latter compound also resembles the phenols in its behaviour towards ammonia.

G. T. M.

Electrolysis of Sodium Chloride. By RICHARD LORENZ and H. WEHRLIN (*Zeit. Elektrochem.*, 1900, 6, 389, 408, 419, 437, 445, and 461).—The authors have made a very elaborate investigation of the electrolysis of saturated solutions of common salt under conditions similar to those which occur in technical practice. The potential differences between platinum electrodes saturated with hydrogen, oxygen, and chlorine, and solutions containing sodium chloride, hypochlorite, hydroxide, and chlorate are also measured. In addition to determining the chemical effects of the current, the authors have made complete measurements of the electrical quantities necessary for an

exact understanding of the process, such as the polarisations at the electrodes, the reverse E.M.F.'s at the electrodes during the passage of the current, &c. The main results arrived at are as follows. The potential difference between an electrode of platinised platinum saturated with hydrogen and a solution of sodium chloride (saturated) + *N* sodium hydroxide is +0.52 volt. (The + sign indicates that the solution is at a higher potential than the electrode). In neutral solutions of salt, the potential difference is +0.12 volt, and the addition of sodium hypochlorite reduces it still further, owing to removal of hydrogen from the electrode, until in a concentrated solution of sodium hypochlorite the potential difference $\text{Pt}/\text{NaOCl} = -1.4$ volts is reached. In the electrolysis of neutral solutions of sodium chloride, the cathodic polarisations found immediately after breaking the circuit vary from -0.6 to -0.98 volt and thus correspond with the potential difference of the hydrogen electrode in solutions containing some hypochlorite. When alkaline solutions of sodium chloride are electrolysed, however, the cathodic polarisation changes sign and has values varying from +0.44 to +0.53 volt, thus again corresponding with the potential of the hydrogen electrode in alkaline solutions.

The E.M.F. required to produce decomposition at the cathode, or the reverse E.M.F. at the cathode during electrolysis, varies from +0.78 to +1.12 volts with polished platinum electrodes, whereas with platinised electrodes it varies from +0.25 to 0.62 volt. The authors conclude, therefore, that the evolution of hydrogen is a reversible process at the platinised cathode, but that a process analogous to supersaturation gives rise to the higher potential difference at the smooth cathodes. The great influence of the presence of sodium hypochlorite on the potential difference of the hydrogen electrode shows clearly the chemical reaction which takes place between hydrogen and hypochlorite at the cathode.

The changes at the anode are more complicated. The potential difference between a platinised platinum electrode saturated with chlorine, and a saturated solution of sodium chloride is about -1.58 volts. The addition of sodium hydroxide to the solution diminishes this value, so that in 2*N* sodium hydroxide the potential difference is -0.935 volt. An oxygen electrode in a saturated solution of sodium chloride gives the potential difference -0.9 volt, whilst in solutions containing sodium hypochlorite the potential difference varies irregularly and independently of the concentration of the hypochlorite from -1.4 to -1.5 volts; this is the potential difference between platinum and sodium hypochlorite solution. This shows that sodium hypochlorite is not oxidised by anodic oxygen, a result which is confirmed by chemical experiments. In the electrolysis of saturated neutral solutions of sodium chloride, the anodic polarisation observed after breaking the circuit varies from -1.66 to -1.53 volts, the lowest values being observed in the solutions containing the most hypochlorite; in alkaline solutions, the values vary from -1.35 to -1.31 volts. These numbers agree well with the potentials of the chlorine electrode in neutral and alkaline solutions, which proves that the anode is always saturated with chlorine even in alkaline solutions. It follows, therefore, that the formation of hypochlorite is due to the action of chlorine on dissolved alkali.

The reverse E.M.F. at the anode during electrolysis is very constant under the most varying experimental conditions. The platinised and smooth anodes give, however, different values, and there is also a very remarkable difference in their chemical behaviour. With a well platinised anode, the reverse E.M.F. is -1.75 volts, which is very nearly the potential of the chlorine electrode in saturated salt solution. The evolution of chlorine is, therefore, almost reversible, and it is found that practically no decomposition of water and no formation of chlorate takes place. With the smooth anodes, the reverse E.M.F. is -2.28 to -2.41 volts in neutral, and -2.26 to -2.3 volts in alkaline solutions. With these anodes, there is a considerable decomposition of water and simultaneous formation of chlorate. At the higher potential reached with the smooth anodes, it is probable that OH ions are discharged along with the chlorine ions, and that the formation of chlorate is due to their combination. The quantity of chlorate formed rises and falls with the potential difference at the anode. T. E.

Combination of Lithium Bromide with Gaseous Ammonia. By J. BONNEFOI (*Compt. rend.*, 1900, 130, 1394—1397. Compare Abstr., 1899, ii, 96).—Dry lithium bromide combines with gaseous ammonia to form four solid highly deliquescent compounds, the properties of which are summarised in the following table :

Composi- tion.	Temperature of formation.	Heat of dissolution.	Heat of formation.	Dissociation pressure.	Vari- ation of entropy $\frac{Q}{T}$
LiBr, NH_3	Above 95°	$+6.857$ Cal. at 15°	$+13.293$ Cal.	730 mm. at 95.5° 806 mm. at 97.5°	0.086
$\text{LiBr}, 2\text{NH}_3$	Between 87° and 95°	$+3.013$ Cal. at 8°	$+25.937$ Cal.	665 mm. at 85° 847 mm. at 90°	0.084
$\text{LiBr}, 3\text{NH}_3$	Between 71.5° and 87°	$+0.287$ Cal. at 10°	$+37.463$ Cal.	636 mm. at 67° 807 mm. at 71.8°	0.33
$\text{LiBr}, 4\text{NH}_3$	About -18°	-1.548 Cal. at 8°	$+48.098$ Cal.	681 mm. at 56° 760 mm. at 58.3°	0.32

The heat developed by combination with the four successive molecules of ammonia is $+13.293$, $+12.644$, $+11.526$, and $+10.635$ Cal., and the relation between these values and the dissociation pressures agrees closely with Clapeyron's formula. The heats of formation given in the above table are the heats of formation from the solid salt and gaseous ammonia. C. H. B.

Lithium Peroxide. By ROBERT DE FORCRAND (*Compt. rend.*, 1900, 130, 1465—1468. Compare this vol., ii, 277, 344, 401, 479).—A hydrated lithium peroxide, $\text{Li}_2\text{O}_2 \cdot \text{H}_2\text{O}_2 \cdot 3\text{H}_2\text{O}$, is precipitated in the form of hard, brilliant, colourless crystals on adding hydrogen peroxide and alcohol to a solution of lithium hydroxide. The heat of solution of this substance is -4.50 Cal., and its decomposition by hydrochloric acid is accompanied by a thermal change of 19.50 Cal.

The anhydrous peroxide, Li_2O_2 , is obtained by drying the above hydrate for 8 days over phosphoric oxide; its heat of solution is 7.19 Cal., whilst its heat of formation from the monoxide is 3.64 Cal.

In the series lithium, calcium, strontium, and barium, the heat of

peroxidation of the monoxide increases, and the heat of formation of the monoxide decreases, as the atomic weight increases; these quantities vary to the same extent, but in opposite sense, and consequently the heat of formation of the peroxide is almost constant, its approximate value being 151. These properties tend to emphasise the relationship existing between lithium and the alkaline earth metals.

G. T. M.

Physical Properties of Cæsium. By MORITZ ECKARDT and EDMUND GRAEFE (*Zeit. anorg. Chem.*, 1900, 23, 378—382).—The following constants were determined: liquid cæsium has a sp. gr. 1·827 at 40° and 1·836 at 27°; solid cæsium has a sp. gr. 1·886 at 26°. The solidifying point is 26·37°; electrical conductivity, 3·63 at 27° (Ag=100); specific heat, 0·04817; atomic heat, 6·406; heat of fusion = 3·73 cal. per 1 gram; contraction on solidification, 0·02637 per 1 c.c. or 2·627 per cent. by volume; coefficient of expansion, 0·0003948.

E. C. R.

Anhydrous Calcium Peroxide and the Constitution of its Hydrates. By ROBERT DE FORCRAND (*Compt. rend.*, 1900, 130, 1388—1391. Compare this vol., ii, 277, 344, 401, 478).—Anhydrous calcium peroxide dissolves in dilute hydrochloric acid with development of +18·93 Cal., and hence $\text{CaO sol} + \text{O} = \text{CaO}_2 \text{ sol.}$ develops +5·43 Cal.

The corresponding values for strontium and barium are +10·875 and +12·10 Cal. respectively, and here the stability of the peroxide and the possibility of preparing it by direct oxidation of the monoxide increase with the atomic weight of the metal, adopting Moissan's value for the heat of formation of calcium monoxide,

$\text{Ca sol.} + \text{O}_2 \text{ gas} = \text{CaO}_2 \text{ sol.}$ develops +150·43 Cal., which is higher than the corresponding value for strontium (+142·075 Cal.). The heats of formation of the hydrates are

$\text{CaO}_2 \text{ sol.} + 8\text{H}_2\text{O liq.} = \text{CaO}_2 \cdot 8\text{H}_2\text{O sol.}$ develops +15·636 Cal.

$\text{CaO}_2 \text{ sol.} + 8\text{H}_2\text{O sol.} = \text{CaO}_2 \cdot 8\text{H}_2\text{O sol.}$ „ +4·196 Cal.

The conversion of $\text{CaO}_2 \cdot 2\text{H}_2\text{O}$ into $\text{CaO}_2 \cdot 8\text{H}_2\text{O}$, however, develops +17·851 Cal., hence the formation of the first compound absorbs -2·215 Cal. This result can only be explained by assuming that $\text{CaO}_2 \cdot 2\text{H}_2\text{O}$ is not a hydrate of calcium peroxide, but a combination of the hydroxide with hydrogen peroxide, $\text{CaH}_2\text{O}_2 \cdot \text{H}_2\text{O}_2$. The heat of formation of this compound from its proximate constituents is -9·815 Cal., and its conversion into the true octohydrate of the peroxide involves changes of opposite signs, the true heat of hydration being +15·636, which corresponds with that of an unstable hydrate.

C. H. B.

Dehydration of Selenite and Hydration of Anhydrite. By V. ZUNINO (*Gazzetta*, 1900, 30, i, 333—339).—Pure precipitated calcium sulphate loses 18 per cent. of its water at 100°, and becomes completely anhydrous at 188°. When heated at 230° in a brisk current of steam, the anhydrous salt absorbs the whole of its water of crystallisation, whilst at 280° the water taken up—only 0·2 per

cent. of the total—is probably mechanically held by the salt. On heating a mixture of sodium chloride and anhydrous calcium sulphate to a white heat for 2 hours, and then cooling the fused mass slowly, small triclinic crystals of anhydrite are obtained. When calcium chloride is used in place of the sodium salt, the residue left after washing the mass with water showed in places signs of setting, which must be due to the conversion of anhydrite into gypsum by hydration. By prolonged boiling in saturated aqueous sodium chloride, the hydrated sulphate is partially converted into anhydrite crystals which by the continued action of water are transformed into gypsum. T. H. P.

Ammonium Earthy Phosphates. By LEONCE BARTHE (*Bull. Soc. Chim.*, 1900, [iii], 23, 422—425).—According to Kippenberger (*Grundlagen Nachweis Giftstoffen*, 1897, 222), the interaction of barium chloride, disodium hydrogen phosphate, and ammonia results in the formation of ammonium barium phosphate, NH_4BaPO_4 . The author is unable to confirm this statement, the precipitate obtained being found to have the composition BaHPO_4 . Attempts to prepare ammonium strontium phosphate were also unsuccessful, only the phosphates $\text{SrH}(\text{PO}_4)$ or $\text{Sr}_3(\text{PO}_4)_2$ being obtained, according to the experimental conditions; these are also formed by the action of methylamine, ethylamine, aniline, or *p*-toluidine on strontium chloride and disodium hydrogen phosphate. Ammonium magnesium phosphate appears to be the only compound of this class capable of existence.

N. L.

Radioactive Barium and Polonium. By FRITZ GIESEL (*Ber.*, 1900, 33, 1665—1668. Compare von Lengyel, this vol., ii, 402; Curie, this vol., ii, 82).—When concentrated uranium nitrate solution is mixed with a little sulphuric acid, then with a solution of a barium salt, care being taken that sufficient barium salt is not added to cause a precipitate, and finally diluted with water, a strongly radio-active precipitate of barium sulphate is obtained. When this sulphate is converted into a soluble barium salt, and this is then treated with ammonium hydroxide, a small amount of precipitate is obtained which is even more strongly radio-active than the original sulphate; but when the barium is subsequently precipitated as carbonate, it has completely lost its activity. The radio-activity is probably due to small quantities of radium, or more probably of actinium.

Polonium preparations obtained from lead chloride from uranium residues have proved to consist of bismuth hydroxide, which, either in this form or as oxychloride, exhibits strong activity. J. J. S.

Bronzes from Ephesus. By KONRAD NATTERER (*Monatsh.*, 1900, 21, 256—262).—A bronze plate (I) and a bronze statue (II) from Ephesus had the following composition:

I. Tin, 8.67; lead, 12.86; zinc, 0.025; copper, 78.77.

II. Tin, 6.09; lead, 4.87; copper, 89.04.

R. L. J.

Lead and Copper Polysulphides. By F. BODROUX (*Compt. rend.*, 1900, 130, 1397—1398).—When a solution of calcium polysulphide is added to an excess of a dilute solution of lead nitrate cooled at 0° and the precipitate is washed with water, alcohol, and, finally, carbon

disulphide, a purple-red polysulphide, PbS_5 , is obtained which decomposes rapidly above 10° into the monosulphide and sulphur.

Cupric acetate under similar conditions yields a brown-red sulphide, Cu_2S_5 , which is fairly stable at the ordinary temperature, but gradually decomposes into the monosulphide and sulphur. Both polysulphides are insoluble in alkali sulphides. C. H. B.

Mercury Chlorosulphide. By F. BODROUX (*Compt. rend.*, 1900, 130, 1398—1399).—When a solution of calcium polysulphide is added to an excess of a cold, saturated solution of mercuric chloride, a chlorosulphide, $\text{Hg}_2\text{S}_5, \text{HgCl}_2$, is obtained as a yellow solid, very stable at the ordinary temperature, but altering superficially when exposed to light. It is insoluble in alkali sulphides, but is blackened and decomposed by alkali hydroxides. When heated, it yields sublimates of sulphur and mercuric chloride; it is completely decomposed by concentrated sodium hypobromite solution, but is not affected by fuming nitric acid at the ordinary temperature. C. H. B.

Action of Water on Mercurous Sulphate. By A. GOUY (*Compt. rend.*, 1900, 130, 1399—1402).—Mercurous sulphate is decomposed by water with formation of a yellow basic sulphate, $\text{Hg}_2\text{O}, \text{Hg}_2\text{SO}_4 + \text{H}_2\text{O}$, which resembles basic mercuric sulphate, but has a marked greenish tinge. Equilibrium is established when the water contains 0.410 gram of mercury and 0.164 gram of sulphuric acid per litre. Water which contains 0.08 gram of sulphuric acid per litre does not convert the normal into the basic salt, and a higher proportion of acid converts the basic salt into the normal. When treated with dilute sulphuric acid, the yellow basic salt becomes white and is thus readily distinguished from basic mercuric sulphate.

Saturated solutions of zinc or cadmium sulphate decompose mercurous sulphate much less readily than water does, but they dissolve more of the unchanged salt. C. H. B.

Unknown Earths contained in Crude Samarium Oxide. By EUGÈNE DEMARÇAY (*Compt. rend.*, 1469—1472. Compare Abstr., 1896, ii, 475).—The author has previously designated by the symbol Σ an unknown element contained in crude samarium oxide and having an atomic weight intermediate between that of samarium and gadolinium. On fractionating the crude samarium oxide by the aid of the double magnesium nitrate method (this vol., ii, 347), a product is obtained containing the unknown element in a highly concentrated form. Certain lines in the spectrum of the element become greatly enhanced as a result of this fractionation, and amongst these are three blue rays considered by Lecoq de Boisbaudran to be characteristic of the hypothetical element Z_e (Abstr., 1893, ii, 323). It therefore seems highly probable that the two elements Σ and Z_e are identical, and the symbol $\Sigma - Z_e$ is proposed for this constituent of crude samarium oxide. The oxide and salts containing the highest percentage of the new element have a pale rose colour and exhibit characteristic absorption, spark, and reversal spectra; the atomic weight obtained by the synthesis of the sulphate is approximately 151.

The paper contains a detailed description of the spectra which is not suitable for abstraction. G. T. M.

Some Properties of Aluminium : Preparation of Hydrogen Phosphide. By CAMILLE MATIGNON (*Compt. rend.*, 1900, 130, 1391—1394).—Aluminium powder freed from grease burns completely in air if strongly heated at one point, the oxide formed being mixed with a small quantity of nitride. If the powdered metal which has begun to burn in air is lowered into a vessel filled with steam, it continues to burn brilliantly, and the liberated hydrogen burns at the mouth of the vessel. Similarly, aluminium powder will burn in carbon monoxide, carbon dioxide, nitric and nitrous oxides, and nitric peroxide, sulphur dioxide, carbon disulphide, the halogens and halogen hydracids, and the vapours of arsenic, antimony, phosphorus, and sulphur chlorides, and also in the vapour of formic acid in the same manner as in steam. With phosphorus, arsenic, antimony, sulphur, and selenium, results were obtained identical with those described by Fonzes-Diacon (this vol., ii, 405).

The phosphide obtained by the action of red phosphorus on the aluminium powder can be used for the preparation of pure hydrogen phosphide, by placing it together with water in a hydrogen apparatus and adding a very small quantity of dilute sulphuric acid. If hydrochloric acid is used, some hydrogen may be liberated. C. H. B.

Composition of Bottle Glasses. By CHR. DRALLE (*Chem. Zeit.*, 1900, 24, 323—328. Compare Zulkowski, *Chem. Ind.*, 1899, 22, 280; 1900, 23, 108).—A number of analyses of modern glasses have been made in order to see whether Zulkowski's conclusions hold good, as these were based on old analyses. The author does not agree with Zulkowski that the whole of the iron and manganese oxides necessarily act as acids; in some cases, as the result of reduction processes, they act as bases. According to Zulkowski, the "saturation coefficient" (that is, equivalents of base/equivalents of acid) of a good non-soluble glass should be 0.333. According to the author, the coefficient may lie between 0.333 and 0.5.

Again, according to Zulkowski, only one alkaline earth may be present in a good glass, but the author finds that the presence of magnesium in addition to calcium does not lower the quality of the glass. J. J. S.

[Preparation of] Permanganic Acid by Electrolysis. By HARMON N. MORSE and J. C. OLSEN (*Amer. Chem. J.*, 1900, 23, 431—443).—A method of preparation of a solution of pure permanganic acid by the electrolysis of its potassium salt is described in detail. Determinations of the conductivity of permanganic acid produced by the electrolysis of the silver salt gave results agreeing closely with those obtained by Lovén (*Abstr.*, 1895, ii, 451), but differing from those of Franke (*Abstr.*, 1895, ii, 252). E. G.

Crystalline Form of the Nickel Sulphate Compound of Hydroxylamine. By RUDOLF UHLENHUTH (*Annalen*, 1900, 311, 127—128).—The compound $\text{NiSO}_4 \cdot 6\text{NH}_2 \cdot \text{OH}$, first described by the

author (Abstr., 1899, ii, 661), belongs to the triclinic system; measurements and a figure are given in the paper. M. O. F.

Silicovanadiomolybdates. I. By CARL FRIEDHEIM and C. CASTENDYCK (*Ber.*, 1900, 33, 1611—1629).—On mixing ammonium vanadate and ammonium silicomolybdate into a paste with water, interaction occurs, and a clear red solution is obtained, the intensity of the colour being greatest when the molecular ratio $(\text{NH}_4)_2\text{O}$, V_2O_5 : $2(\text{NH}_4)_2\text{O}$, SiO_2 , 12MoO_3 , $8\text{H}_2\text{O}$ is 2:1; from a solution prepared in this way, an *ammonium silicovanadiomolybdate*, $3(\text{NH}_4)_2\text{O}$, SiO_2 , V_2O_5 , 11MoO_3 , $27\text{H}_2\text{O}$, separates in lustrous, red, well-formed crystals, often 2 cm. in length. These crystals are easily soluble in water, and during their formation become contaminated by sparingly soluble ammonium vanadiomolybdates of varying composition, the latter being separated mechanically. The composition of these ammonium vanadiomolybdates, according to the order of their separation, is as follows: (1) $2(\text{NH}_4)_2\text{O}$, $2\text{V}_2\text{O}_5$, 5MoO_3 , $8\text{H}_2\text{O}$, yellow; (2) $(\text{NH}_4)_2\text{O}$, V_2O_5 , 2MoO_3 , $4\text{H}_2\text{O}$, yellowish-green; (3) $2(\text{NH}_4)_2\text{O}$, $3\text{V}_2\text{O}_5$, 4MoO_3 , $11\text{H}_2\text{O}$, bright brown; (4) $(\text{NH}_4)_2\text{O}$, $2\text{V}_2\text{O}_5$, 2MoO_3 , $8\text{H}_2\text{O}$, reddish-brown; (5) $4(\text{NH}_4)_2\text{O}$, $12\text{V}_2\text{O}_5$, 5MoO_3 , $24\text{H}_2\text{O}$, brownish-red. The first three of these are microcrystalline, whilst the two last form felted needles.

On recrystallising the foregoing ammonium silicovanadiomolybdate from water, either hot or cold, decomposition occurs, and a series of new compounds, (1) $3(\text{NH}_4)_2\text{O}$, SiO_2 , V_2O_5 , 9MoO_3 , $20\text{H}_2\text{O}$; (2) $3(\text{NH}_4)_2\text{O}$, SiO_2 , V_2O_5 , 10MoO_3 , $21\text{H}_2\text{O}$; (3) $3(\text{NH}_4)_2\text{O}$, SiO_2 , V_2O_5 , 15MoO_3 , $24\text{H}_2\text{O}$, is obtained; these differ little from the parent substance and from one another in colour and crystalline form, but are differentiated by the behaviour of their saturated solutions with silver, lead, and mercurous nitrates. The following table gives their principal physical properties:

Ammonium silicovanadiomolybdate, $(\text{NH}_4)_2\text{O}:\text{SiO}_2:\text{V}_2\text{O}_5:\text{MoO}_3$	Sp. gr. of solid at 18°.	Sp. gr. of saturated sol. at 18°.	Solubility in grams per c.c.
3:1:1:9+20H ₂ O	2·8020	1·21322	0·32016
3:1:1:10+21H ₂ O	2·8044	1·25275	0·35026
3:1:1:11+27H ₂ O	2·8074	1·29266	0·38086
3:1:1:15+24H ₂ O	2·8162	1·43761	0·48997

It is noteworthy that the addition of each mol. of molybdenum trioxide causes a regular increase of approximately 0·00237 unit in the sp. gr. of the solid salt; 0·037 unit for the sp. gr. of the saturated solution, and 0·030 unit for the solubility. The salts containing 9MoO_3 and 15MoO_3 can be recrystallised unchanged from water, but that containing 10MoO_3 yields a mixture of the other three salts.

On adding potassium chloride to cold saturated solutions of these ammonium salts, crystalline compounds are precipitated which owe their origin to the replacement of $2\text{K}_2\text{O}$ for $2(\text{NH}_4)_2\text{O}$ in the parent substances; the following table gives their physical properties:

Composition.	Sp. gr. of solid.	Sp. gr. of sat. sol. at 18°.	Solubility in grams per c.c.
$(\text{NH}_4)_2\text{O}, 2\text{K}_2\text{O}, \text{SiO}_2, \text{V}_2\text{O}_5, \left. \begin{array}{l} 9\text{MoO}_3, 20\text{H}_2\text{O} \end{array} \right\}$	2.8648	1.17031	0.24021
$(\text{NH}_4)_2\text{O}, 2\text{K}_2\text{O}, \text{SiO}_2, \text{V}_2\text{O}_5, \left. \begin{array}{l} 10\text{MoO}_3, 21\text{H}_2\text{O} \end{array} \right\}$	2.8682	1.19184	0.25914
$(\text{NH}_4)_2\text{O}, 2\text{K}_2\text{O}, \text{SiO}_2, \text{V}_2\text{O}_5, \left. \begin{array}{l} 11\text{MoO}_3, 12\text{H}_2\text{O} \end{array} \right\}$	2.8704	1.21378	0.27914
$(\text{NH}_4)_2\text{O}, 2\text{K}_2\text{O}, \text{SiO}_2, \text{V}_2\text{O}_5, \left. \begin{array}{l} 15\text{MoO}_3, 14\text{H}_2\text{O} \end{array} \right\}$	2.8803		

Similar laws to those obtaining in the case of the original ammonium compounds regulate the change of sp. gr. and solubility of these salts; moreover, the replacement of 4K for 4NH₄ in the original salts increases the sp. gr. in each case by a constant amount equal to 0.0634 unit. On the other hand, the difference between the sp. gr. of saturated solutions of the corresponding ammonium and potassium salts increases by approximately 0.02 unit for each addition of 1MoO₃, whilst a similar increase of 0.01 unit is observed in the solubility. W. A. D.

Preparation of some Uranium Oxides. By JULES ALOY (*Bull. Soc. Chim.*, 1900, [iii], 23, 368—370).—Uranous oxide, UO₂, is obtained in the form of microscopic, black crystals by heating crystallised uranic hydroxide in a current of hydrogen. When thus prepared, it is not pyrophoric, and is only slowly converted into the green oxide by heating to redness. The violet hydrate of uranoso-uranic oxide, U₃O₈, which Ebelmen prepared by exposing to sunlight a solution of uranium oxalate, is more readily obtained, in a similar manner, from an alcoholic solution of the acetate, or from a mixture of the aqueous solution of the acetate with ether; it could not be obtained crystalline. The violet hydrate is readily oxidised to uranic hydroxide by exposure to air, and when boiled with water it yields orthorhombic crystals of the composition UO₃·H₂O, which are stable in dry air at 100°. A crystallographic study of these crystals has been made by Bertrand. N. L.

Compounds of Uronic Acid with Sulphurous Acid. By VOLKMAR KOHLSCHÜTTER (*Annalen*, 1900, 311, 1—25).—The simplest compound of uranium trioxide with sulphur dioxide was first obtained by Girard (*Compt. rend.*, 1852, 34, 22) from the action of aqueous sulphurous acid on uranic acid, and is also produced when sulphur dioxide is passed into solutions of uranyl acetate and uranyl nitrate. It is a pale green, crystalline substance, forming minute, slender needles which exhibit double refraction. The composition is expressed by the formula UO₃·SO₂·4H₂O, and when exposed to a temperature of 105° during an hour, the substance loses 3½H₂O.

The compounds, 2UO₃·3SO₂·R₂O, prepared by dissolving the foregoing substance in much sulphurous acid, and adding an alkali hydrogen sulphite to the solution heated on the water-bath, are identical with compounds obtained by Scheller (*Annalen*, 1867, 144, 238), who ascribed to them the erroneous formula UO₂·OR, SO₃H; the *potassium*, *ammonium*, and *sodium* derivatives of this substance are described.

When uranyl sulphite, $\text{UO}_3 \cdot \text{SO}_3 \cdot 4\text{H}_2\text{O}$, is heated on the water-bath with aqueous sulphurous acid in amount insufficient to dissolve it, large, golden-yellow prisms separate; this *compound* has the empirical formula, $\text{UO}_3 \cdot \text{SO}_3 \cdot 2\frac{3}{4}\text{H}_2\text{O}$, and loses $2\frac{3}{4}\text{H}_2\text{O}$ when heated at 105° .

The *compounds*, $4\text{UO}_3 \cdot 5\text{SO}_3 \cdot \text{R}_2\text{O} + x\text{H}_2\text{O}$, is prepared by adding an alkali hydrogen sulphite to uranyl nitrate, filtering the amorphous precipitate, and heating it on the water-bath with aqueous sulphurous acid in quantity insufficient for dissolution; the *potassium*, *ammonium*, and *sodium* derivatives of this substance are described.

The *compounds*, $3\text{UO}_3 \cdot 2\text{SO}_3 \cdot \text{R}_2\text{O}$, produced by the action of water on the foregoing substances, are orange-yellow, crystalline salts; the *potassium*, *ammonium*, and *sodium* derivatives have been prepared.

The *compounds*, $\text{UO}_3 \cdot 2\text{SO}_3 \cdot \text{R}_2\text{O}$, obtained by passing sulphur dioxide through uranyl nitrate to which excess of alkali hydroxide has been added, separate from the clear, dark yellow liquid in crystalline crusts; the *ammonium* and *potassium* derivatives have been prepared.

Constitutional formulæ for these compounds are suggested by the author. M. O. F.

Mode of Decomposition of Certain Metallic Perchlorides. By WILLIAM OECHSNER DE CONINCK (*Compt. rend.*, 1900, 130, 1551—1552).—Auric, platonic, and ferric chlorides are decomposed when their aqueous solutions are filtered through animal charcoal, the metals being completely retained by the filter whilst the acid radicle remains in the filtrate. Similar results were obtained with saw-dust, brick-dust, and coarse or fine grained coke-dust; fine sand, on the other hand, has no action on the perchlorides. This mode of decomposition does not obtain with ferrous chloride, and its nickel, cobalt, manganese, zinc, copper, and magnesium analogues; stannous chloride in dilute hydrochloric acid undergoes oxidation and the oxychloride produced is completely absorbed by the animal charcoal. G. T. M.

Platinum Compounds of Hydroxylamine. By RUDOLF UHLENHUTH (*Annalen*, 1900, 311, 120—126).—The *platinum base*, $\text{Pt}(\text{NH}_2 \cdot \text{OH})_4(\text{OH}_2)$, prepared by treating hydroxylamine (12 mols.) with hydroplatinichloric acid (1 mol.) in dilute aqueous solution, boiling the liquid till colourless, and allowing it to cool slowly, separates in slender, snow-white needles, insoluble in water, alcohol, or ether, but readily soluble in dilute mineral acids, acetic acid, or formic acid. Cold dilute nitric acid dissolves it, and when heated, decomposes it completely. When heated at 173° , the dry base explodes and becomes ignited. The *sulphate*, $\text{Pt}(\text{NH}_2 \cdot \text{OH})_4\text{SO}_4$, forms large, triclinic crystals containing $1\text{H}_2\text{O}$. The *hydrochloride*, $\text{Pt}(\text{NH}_2 \cdot \text{OH})_4\text{Cl}_2$, crystallises in flat needles; the action of dilute hydrochloric acid on the base also gives rise to the yellow *salt*, $\text{Pt}(\text{NH}_2 \cdot \text{OH})_2\text{Cl}$, which forms long, golden-yellow needles, and the blue *salt*, $\text{Pt}(\text{NH}_2 \cdot \text{OH})_2\text{Cl}_2$, which crystallises in blue needles. The *nitrate* forms lustrous, colourless needles. M. O. F.

Mineralogical Chemistry.

Roumanian Petroleums. By LAZAR EDELEANU and G. A. FILITI (*Bull. Soc. Chim.*, 1900, [iii], 23, 382—403).—The first part of this preliminary paper deals with the chemical composition of Roumanian petroleums. These consist principally of carbon and hydrogen, but small quantities of oxygen are often found, especially in the denser varieties from Matita and Sarata, owing to the presence of compounds of an acid character which are extracted from the oil by alkalis. In some specimens, traces of nitrogen and sulphur are found, the latter possibly in the form of compounds analogous to thiophen. A sample of petroleum from Berka (Buzen), having a sp. gr. 0·824 at 15°, was specially examined with the object of ascertaining the nature and amount of benzene hydrocarbons contained therein. From the results obtained by fractionally distilling the oil, treating the separate fractions with nitric acid, and isolating the nitro-derivatives thus produced, the presence of considerable quantities of benzene, toluene, *m*-xylene, mesitylene, and probably higher homologues, was proved. Nearly all the Roumanian petroleums examined were found to contain hydrocarbons of the benzene series, some only in very minute quantities, as with the oils from Casin and Recea, and others in much larger proportions, as was the case with oils from Campeni-Parjol, Colibasi, &c.

In the second part of the paper the physical and technical properties are dealt with, and the results obtained from 36 specimens of petroleum from the provinces of Dambovita, Buzeu, Prahova, and Bacau, are recorded in five tables. The colour of the oils varied from clear yellow to opaque brown or black, and all exhibited a greenish fluorescence. The sp. gr. at 15° ranged from 0·7833 to 0·9050, the boiling point from 25° to 62°, and the viscosity at 20° (water at 20° = 1) from 1·04 to 4·88, but usually lay between 2·00 and 2·80. The odour was in most cases feebly ethereal and agreeable, but some specimens had a strong alliaceous odour and others an odour of hydrogen sulphide. The flash point, as determined with the Abel-Pensky apparatus, was almost always below 0°. The behaviour of the oils on distillation was carefully studied and the characters of the various products examined. The best light oils are yielded by petroleums from Campeni-Parjol, Casin, Poiana, Plopeni, and Predeal Berka, whilst the Gura Ocniti, Tintea, and Sarata petroleums are richest in heavy, high boiling oils.

N. L.

Minerals from the Bogoslowsk District, Urals. By EUGRAPH S. VON FEDOROFF and W. W. NIKITIN (*Ann. Geol. Min. Russie*, 1899, 3, 79—91, 91—103).—A description is given of several mineral species from the Bogoslowsk mining district, where ores of copper and iron are won. Analyses are given of the following.

Quartzine in the form of microscopic spherulites, with a little bright green chloritic mineral in the interspaces, occurs as blocks embedded in diabase on the river Kakwa. Analysis gave :

SiO ₂ .	Al ₂ O ₃ , FeO ₂ .	CaO.	MgO.	H ₂ O.
90·83	5·25	0·33	0·29	2·1

Garnet from augite-garnet rocks gave I for the resin-brown, and II for the pale greenish crystals.

	SiO ₂ .	Fe ₂ O ₃ .	Al ₂ O ₃	Mn ₂ O ₃ .	FeO.	CaO.
I.	34·98	23·77	3·32	1·22	3·33	34·06
II.	38·22	25·62	2·11	0·58	1·96	31·80

Datolite occurring as a crust on the walls of a diabase dyke gave, on analysis by Januschewitsch :

SiO ₂ .	Al ₂ O ₃ , Fe ₂ O ₃ .	CaO.	MgO.	H ₂ O, CO ₂ .	B ₂ O ₃ .
36·77	0·31	33·78	1·5	8·4	[19·24]

Muschketowitz is the name given to a pseudomorph of magnetite after hæmatite; it has the platy structure of hæmatite, but a black streak, and is strongly magnetic with polarity. The analysis (Fe₂O₃, 75·35; FeO, 19·88; H₂O, 0·31; insol., 4·4) shows that the change from hæmatite to magnetite has not been quite complete.

Marsjatskite is the name given to a manganglauconite which forms the bulk of a Tertiary sandstone in the Marsjat forest; the microscopic grains are amorphous, and have a very pale green tint. A partial analysis of the rock, which also contains grains of quartz and other minerals, gave: SiO₂, 20·94; Fe₂O₃, 8·78; Mn, 25·66 per cent. On exposure to air, the material is easily altered, giving rise to workable deposits of manganese ores containing 35—40 (max. 50) per cent. of manganese.

L. J. S.

Jadeite from Piedmont. By GIUSEPPE PIOLTI (*Jahrb. Min.*, 1900, i, Ref. 341; from *Atti Accad. Sci. Torino*, 1899, 34, 600—608. Compare Abstr., 1898, ii, 525).—A green pebble found in a moraine at the entrance of the Susa Valley, near Rivoli, has the characters of jadeite. Sp. gr. 3·407. The results of the analysis differ considerably from those required by the jadeite formula, NaAl(SiO₃)₂, but agree with those of an analysis by Damour of Asiatic jadeite :

SiO ₂ .	Al ₂ O ₃ .	Fe ₂ O ₃ .	Cr ₂ O ₃ .	CaO.	MgO.	Na ₂ O.	Loss on ignition.	Total.
55·11	9·66	7·55	trace	12·04	7·33	7·84	0·33	99·86

Only one pebble was found, and the original locality of the material is not known. This occurrence is discussed in connection with the neolithic jade implements of Central Europe.

L. J. S.

Minerals from the Radauthal, Harz. By JOHANNES FROMME (*Jahresber. Ver. Naturwiss. Braunschweig*, 1900, 12, 31—42).—Descriptions are given of several minerals from the gabbro and the pegmatite of the Radauthal near Harzburg in the Harz.

Cavities between the gabbro and pegmatite are filled with calcite and a chloritic mineral; the latter, which is referred to chalcodite, occurs as scaly to granular masses of a greyish-green colour; sp. gr. 2·44. It is easily decomposed by hydrochloric or sulphuric acid, with separation of flocculent silica. The following is the mean of two analyses made on material separated from calcite by the action of acetic acid. Direct determinations of the iron on unprepared material gave Fe₂O₃, 4·82; and FeO, 28·20 per cent.

SiO ₂ .	Al ₂ O ₃ .	Fe ₂ O ₃ .	FeO.	MnO.	CaO.	MgO.	H ₂ O.	K ₂ O, Na ₂ O.	Total.
47.15	4.49	9.00	24.60	1.49	0.50	3.71	8.70	traces	99.64

L. J. S.

Weathering of Diabase in Virginia. By THOMAS L. WATSON (*Amer. Geologist*, 1899, 24, 355—369. Compare Abstr., 1898, ii, 612).—Analyses are given of the fresh and altered rock from a dyke adjacent to the one previously described, and similar results are obtained.

L. J. S.

Meteorite from Ergheo, Somaliland. By ETTORE ARTINI and GILBERTO MELZI (*Jahrb. Min.*, 1900, i, Ref. 357—360; *Soc. d'Esplorazione Commerciale in Africa*, Milan, 1898, 12 pp., and *Rend. R. Ist. Lombardo*, 1898, [ii], 31, 983—994).—This stone fell in July, 1889, at Ergheo, near Brava, in the Somali peninsula; it weighs 20,375 grams, but was originally somewhat larger. Sp. gr. 3.31. Chondrules of olivine or of enstatite or of both are set in a crystalline ground mass of olivine and enstatite; troilite, metallic nickel-iron, magnetite, glass, maskelynite, and possibly feldspar are also present. Analysis by G. Boeris gave the following results:

Metallic Fe.	Ni + Co.	FeS.	Sol. in HCl.	Insol. in HCl.	Total.
0.57	0.17	9.48	56.50	32.73	99.45

	SiO ₂ .	FeO.	Al ₂ O ₃ .	CaO.	MgO.	Na ₂ O, K ₂ O.	Total.
Sol. in HCl	23.69	12.95	0.56	0.71	18.59	—	56.50
Insol. in HCl	57.62	12.79	5.11	1.13	23.06	0.41	100.12

L. J. S.

Meteoric Iron from Morradal, Norway. By EMIL W. COHEN (*Jahrb. Min.*, 1900, i, Ref. 354; *Videnskabs-Selskabets Skrifter, Christiania*, 1898, Class I, No. 7, 12 pp.).—This iron was found at Morradal near Grjotli, between Skiaker and Stryn; it weighs 2750 grams. It belongs, with the irons from Smithland and Babb's Mill, to the group of ataxites rich in nickel. Analysis by O. Sjöström gave:

Fe.	Ni.	Co.	Cu.	Cr.	P.	S.	Sp. gr.
79.67	18.77	1.18	0.06	0.06	0.18	0.27	7.8543

This corresponds with the following mineralogical composition: nickel-iron, 98.12; schreibersite, 1.17; troilite, 0.55; daubreelite, 0.16.

L. J. S.

Mineral Water from the Cold or "Park" Spring at Evaulles-Bains (Creuse). By EDMOND BONJEAN (*Bull. Soc. Chim.*, 1900, [iii], 23, 405—407).—This is a saline, alkaline water containing 1.492 grams of solid matter per litre and having a temperature of 8°; minute quantities of lithium, manganese, arsenic, and fluorine were detected.

N. L.

Mineral Water from the Brault No. 3 Spring at Sail-sous-Couzan (Loire). By EDMOND BONJEAN (*Bull. Soc. Chim.*, 1900, [iii], 23, 408—409).—The water contains 2.1305 grams per litre of solid

matter, consisting chiefly of sodium, potassium, calcium, and magnesium carbonates; it is remarkable for the large quantity of free carbon dioxide it contains, namely, 1438 c.c. per litre. N. L.

Waters of Salsomaggiore. By RAFFAELE NASINI and FRANCESCO ANDERLINI (*Gazzetta*, 1900, 30, i, 305—333).—The mineral constituents of these waters consist mainly of sodium and calcium chlorides, small quantities of a large number of other salts being also present. They are very rich in bromine and iodine, and contain a larger proportion of strontium and lithium than any other known natural water; the quantities of these constituents in grams per litre of the water from the spring “delle Saline” are Br, 0.26411; I, 0.06050; Sr, 0.42780; Li, 0.12152. The dissolved gases, present to the extent of 20.64 c.c. per litre, consist principally of methane, ethane, and carbon dioxide, with smaller quantities of heavy hydrocarbons, nitrogen and oxygen (compare this vol., ii, 415). T. H. P.

Physiological Chemistry.

Action of Morphine on Respiration. By HUGO WINTERNITZ (*Pflüger's Archiv*, 1900, 80, 344—350. Compare this vol., ii, 221).—Polemical. The work of, and conclusions drawn by, Impens (this vol., ii, 28) are criticised. W. D. H.

Rôle of Purine Substances in Human Metabolism. By RICHARD BURIAN and HEINRICH SCHUR ((*Pflüger's Archiv*, 1900, 80, 241—343).—Every healthy adult excretes a certain characteristic amount of alloxuric or purine substances, which is independent of his diet. This is the result of tissue metabolism, and may be termed 'endogenous urinary purine.' Its amount may be directly estimated by examining the urine after a diet of substances which are practically free from purine compounds (milk, white bread, potatoes, rice, green vegetables, eggs, and cheese). Examination of the urine during hunger does not give trustworthy results; but on ordinary diet, the amount of urinary purine is increased by a part of the 'nutrition purine, and this may be termed 'exogenous urinary purine.' The nutrition purine does not pass wholly into the urine; a certain fraction remains in the organism, the purine double ring being broken down. The amount of the remainder (exogenous urinary purine) differs for different forms of food, and is but little affected by the individuality of the subject of the experiment. The following table gives some of the figures quoted:

Diet.	Total percentage of purine substances in diet.	Percentage of exogenous urinary purine.
Beef and veal	0·06	0·03
Coffee	0·2	0·075
Calf's liver	0·12	0·06
Calf's spleen.....	0·16	0·08
Calf's thymus	0·4	0·1

By subtracting the exogenous from the total urinary purine, the endogenous urinary purine is obtained, and the results agree closely with the numbers obtained by direct estimation; it varies in the majority of people from 0.1 to 0.2 gram daily; but higher and lower values were obtained. W. D. H.

Use of Horse-flesh as Food. By EDUARD PFLUGER (*Pflüger's Archiv*, 1900, 80, 111—138).—Horse-flesh by itself causes digestive disturbances, especially diarrhoea. This is partly, but not wholly, explained by the poorness of the tissue in fat. There is, however, besides, some toxic material in the flesh, which is removed by extraction with hot water or alcohol; it is not soluble in ether. It was not further identified. Horse-flesh, before it is eaten, should, therefore, be extracted with hot water, and mixed with either mutton or beef fat; these solid fats are better than that of the pig. The modern view of fat absorption, namely, that hydrolytic decomposition of the fat is necessary, is supported. W. D. H.

NOTE BY ABTRACTOR.—Pflüger's experiments were made on dogs, but recent experiences during the siege of Kimberley have led to the same result. The necessity of mixing the horse-flesh with beef suet was well known to the medical men in South Africa.—W. D. H.

Sugar as Food. By FRIEDRICH STROHMER (*Bied. Centr.*, 1900, 29, 172—174; from *Oest. Ung. Zeit. Zuckerind. Landw.*, 1899, Heft 3).—The importance of sugar as food is indicated by the fact that in human milk lactose is the most prominent constituent, and the results of Soxhlet and Biedert's experiments showed that sucrose is at any rate not inferior to lactose.

According to Schumburg, even small amounts of sugar (30 grams) will renew the power of muscles, tired by work, in half or three-quarters of an hour. Sugar is accordingly specially suited for the production of muscular force, this property being increased by the action of sugar on the nervous system in overcoming the feelings of fatigue.

Excessive consumption of sugar is to be avoided, as digestion would be interfered with; no injury to the teeth will result, as is frequently supposed. When properly employed, sugar is of great value as food, especially after bodily exertion. N. H. J. M.

Mineral Statics of the Human Fœtus during the last Five Months of Intrauterine Life. By LOUIS HUGOUNENQ (*Compt. rend.*, 1900, 130, 1422—1424).—Sodium chloride is assimilated by the human fœtus chiefly at the beginning and during the middle period of gestation, but the assimilation of this compound falls off markedly towards the end of the period. During the second half of gestation, the assimilation of phosphoric acid is very regular, but increases somewhat towards the end, whilst the assimilation of calcium increases very markedly towards the end and becomes relatively greater than that of phosphoric acid, the excess being found in the ash in the form of calcium carbonate. With these exceptions, the assimilation of inorganic constituents is almost constant during the last five months, although there is a marked increase in the total weight towards the

end. The cellule of the embryo at four months has practically the same requirements, as regards inorganic food, as the cellule at the end of gestation. The maximum rates of assimilation of sodium chloride on the one hand, and of phosphoric acid and calcium on the other, correspond respectively with the genesis of the red corpuscles and of the osseous system.

C. H. B.

Rôle of Iron in Blood Formation. By A. HOFMANN (*Virchow's Archiv*, 1900, 160, 235—306).—Iron in various forms of organic and inorganic combination is absorbed in the duodenum, and is carried in union with proteid in the 'transport' cells of the blood to the spleen, liver, and especially to the bone marrow. The principal use of the metal is to act as a stimulus to the red marrow. It causes an increase in the growth and activity of this tissue, and so leads to an increased formation of the blood discs. In chlorosis, the bone marrow becomes comparatively inactive.

W. D. H.

Action of Oxygen on the Excised Mammalian Heart. By GÜNTHER STRECKER (*Pflüger's Archiv*, 1900, 80, 161—175).—A new apparatus is described and figured for artificially feeding an excised mammalian heart. The most important result of the experiments recorded is the importance of oxygen in the nutritive fluid. Blood containing carboxyhæmoglobin soon brings the heart to a standstill, not because carbon monoxide is a poison to the organ, for it still remains excitable, but because it contains no free or readily dissociable oxygen. Fresh arterial blood will set such a heart beating again. This need of oxygen for cardiac activity has been previously insisted on by Yeo (*J. Physiol.*, 1885, 6, 535), and more recently in connection with the mammalian heart by Porter (*Amer. J. Physiol.*, 1898, 1, 511).

W. D. H.

Value of Calcium and Potassium Ions in Cardiac Activity. By JACQUES LOEB (*Pflüger's Archiv*, 1900, 80, 229—232).—The conclusion is drawn that calcium and potassium ions are unnecessary for the maintenance of cardiac and other rhythmical actions, but their usefulness is indirect in neutralising the poisonous action of the sodium chloride which is present in the blood and in sea water.

W. D. H.

Elementary Composition and Heat of Combustion of Human Fat. By FRANCIS GANO BENEDICT and EMIL OSTERBERG (*Amer. J. Physiol.*, 1900, 4, 69—76).—The composition of human fat appears to be remarkably constant; the average of twenty-four determinations gives hydrogen, 11.78, and carbon, 76.08 per cent. The heat of combustion averages 9.523 cal. per gram.

W. D. H.

Preparation of Pure Glycogen. By ERNST BENDIX and JULIUS WOHLGEMUTH (*Pflüger's Archiv*, 1900, 80, 238—240).—Glycogen prepared by Pflüger's modification of Külz's method gives the phloroglucinol and orcinol reactions for pentoses. This is due to an admixture with a pentose or pentosan, for after repeated solution in hot water and precipitation by alcohol, the reaction is lost. After treatment of the impure glycogen with hydrochloric acid, and removal

of the greater part of the sugar so formed by fermentation with yeast, the product yields two osazones, one of which is hexosazone, from the remains of the sugar not decomposed by the yeast; the other, which melts at 153—155°, has all the characters of pentosazone. The source of the pentose is believed to be the nucleo-proteid of the liver; indeed, the glycogen is usually contaminated with nuclein.

W. D. H.

Physiology of the Suprarenal Capsules. By BENJAMIN MOORE and C. O. PURINTON (*Amer. J. Physiol.*, 1900, 4, 51—56, 57—59).—The cause of the death which often supervenes within 24 hours after extirpation of the suprarenals is obscure. In cats, cardiac thrombosis is, however, frequently found. A predisposing condition for the ready occurrence of intravascular clotting is to be found in the enfeeblement of the circulation.

The large relative size of these organs in foetal animals is not found in all animals, as, for example, in the cat. In the human embryo and new-born child, the glands are comparatively large, but their medulla contains neither chromogen nor active physiological principle. In the embryonic ox and goat, both appear to be present.

W. D. H.

Alimentary Oxaluria. By GALILEO PIERALLINI (*Virchow's Archiv*, 1900, 160, 173—185).—The soluble and insoluble salts of oxalic acid, the latter in smaller degree, are absorbed, and pass as calcium oxalate into the urine. Foods containing excess of oxalates cause the excretion to increase. The absorption of such insoluble oxalates as that of calcium can hardly be explained as the result of the action of the dilute acid of the gastric juice, but is attributed to decomposition, brought about by the presence of alkali carbonates in the intestine.

W. D. H.

Action of certain Renal Poisons. By W. LINDEMANN (*Ann. Inst. Pasteur*, 1900, 14, 49—59).—This records the commencement of a research on poisons which affect the kidneys, and aims at the elucidation of the manner in which the toxins in serum, and in such diseases as scarlet fever, bring about renal disorder. The special poison here investigated is vinylamine, and the experiments were performed on mice, rabbits, and dogs, some of which were rapidly killed with fatal doses, and others subjected to chronic poisoning. In immediately fatal cases, the main effects in the kidney are explicable by anæmia. In the more chronic cases, the urine is dilute, highly albuminous, and contains casts and epithelial débris; the kidneys show signs of acute nephritis. The interstitial connective tissue is not affected. Certain toxic serums produce somewhat similar results.

W. D. H.

Chemistry of Vegetable Physiology and Agriculture.

Fermentation of Cellulose. By V. OMELIANSKY (*Chem. Centr.*, 1900, i, 918—919; from *Arch. Sci. biolog. St. Petersb.*, 7, 411—434. Compare Abstr., 1898, i, 291).—The morphological properties of *Bacillus fermentationis cellulose* are described in the original paper. Cellulose is attacked by this organism in solutions which contain only mineral salts, the fermentation being effected through a series of changes, by which the specific ferment is gradually purified, and eventually left as a pure culture. The cellulose yields 70 per cent. of fatty acids, acetic acid, and butyric acid, and 30 of gases (carbon dioxide and hydrogen); methane is only formed in the last phases, and is possibly due to the action of another microbe. Hoppe-Seyler's fermentation of cellulose in which carbon dioxide and marsh gas are formed, but no solid or liquid products, is probably effected by a bacillus which has not yet been isolated; this bacillus is probably not the amylobacterium. E. W. W.

Identity of the Ærogenic Bacillus of Milk with the Pneumobacillus of Friedländer. By LEON GRIMBERT and G. LEGROS (*Compt. rend.*, 1900, 130, 1424—1425).—The ærogenic bacillus of milk and the pneumo-bacillus of Friedländer agree in the following characteristics, and seem to be completely identical; they are immobile, do not liquefy gelatin, and do not produce indole in culture fluids containing peptone, but ferment various carbohydrates, yielding products which vary with the nature of the sugar; and they produce capsules in the blood of animals inoculated with them. C. H. B.

Action of the Bacillus Anthracis on Carbohydrates. By MDLLE. NAPIAS (*Ann. Inst. Pasteur*, 1900, 14, 232—248).—The anthrax bacillus attacks starchy and saccharine materials, yielding lactic and acetic acids. The latter acid is believed to be formed from the former. In virulent species, proteolytic properties are dominant, and in attenuated specimens amylolytic action is predominant.

W. D. H.

Proteolysis produced by Aspergillus Niger. By G. MALFITANO (*Ann. Inst. Pasteur*, 1900, 14, 60—81).—The secretion of a proteolytic enzyme is constant during the life of *Aspergillus niger*, and is chiefly associated with the death of the cells. It is believed that such agents will not only produce effects on the surrounding medium, for instance, the liquefaction of gelatin, but also in the protoplasm of the cells carry out the work of disassimilation.

W. D. H.

Resolution of a Racemic Compound by means of Moulds. By C. ULPANI and S. CONDELLI (*Gazzetta*, 1900, 30, i, 382—394).—Results are given of a number of experiments made to determine the conditions best suited for the resolution of a racemic compound into its optically active isomerides by means of moulds. The spores of

Aspergillus niger do not develop in absence of oxygen, but they are not killed, unless indeed by a very long exposure in a vacuum. This mould attacks a racemic compound more energetically in presence of a small quantity of oxygen than when a larger quantity is present, but at the same time less of the optically active isomeride is obtained, since Pfeffer's economic coefficient, that is, the ratio of material consumed to that formed, has a greater value when there is a deficiency in the oxygen employed. The life, and hence also the activity, of moulds are almost entirely inhibited by sunlight, and the rapidity with which a racemic compound is resolved increases as the luminosity decreases, and increases also with the temperature. Experiments with racemic, lactic, and mandelic acids and alanine show that *Penicillium glaucum* flourishes best in solutions of greater concentration and less acidity than is the case with *Sterigmatocystis niger*. The proportion of inorganic salts necessary for the complete development of moulds is very small, the small quantity dissolved from the glass vessel containing the solution being sufficient. On growing *Sterigmatocystis niger* in 5 litres of solution containing 120 grams of crystallised racemic acid and small quantities of ammonium, potassium, and magnesium salts, it was found that in the first period, extending to the end of the 32nd day, *d*-tartaric acid was almost exclusively destroyed; after this, the destruction of the dextro-acid continued, and was completed after a further 33 days, 27 per cent. of the total lævo-acid being also destroyed; during the third period, from the 65th to the 123rd day, the fermentative process became weaker, since, besides the last traces of dextro-acid, only 7 per cent. of the initial quantity of lævo-acid was destroyed. After this, no further appreciable action took place, although the mould was found to be capable of vigorous growth in a suitable medium. From the residual liquid, only potassium hydrogen *l*-tartrate could be separated, and in a solution of this salt, as stated by Pfeffer, no development of *Aspergillus niger* is possible. T. H. P.

Denitrification. By ALBERT STUTZER and HJALMAR JENSEN (*Bied. Centr.*, 1900, 29, 268—273; from *Centr. Bakt.*, 1897, 622 and 698).—The results of experiments with pure cultures of various denitrifying bacteria on the utilisation of carbon compounds, showed that citric acid alone is sufficient to supply the necessary carbon. Dextrose alone is unsuitable, and in presence of citric acid even somewhat retards growth; it is, however, not altogether useless; there is a connection between the nitrate destroyed and the carbon compounds used up in solutions which contain, besides sugar, citric acid. In such solutions, continued addition of nitrate soon stops denitrification, which is, however, renewed on adding more sugar.

Glycerol and starch (compare Déherain, *Abstr.*, 1899, ii, 511) do not produce fermentation, either separately or together; but a mixture of glycerol and a citrate is suitable. Lactic and butyric acids, but not formic acid, are very good sources of carbon when employed in Giltay and Aberson's solution, in the place of citric acid.

When, instead of pure cultures, garden soil is employed, glycerol is decomposed by putrefaction bacteria, and the products are utilised by

denitrifying bacteria. Similar, and still more decided, results were obtained with straw.

The value of stable manure as nitrogenous manure diminishes as the amount of carbonaceous matter available for denitrifying bacteria increases. When fresh manure is ploughed in late, the yield of the succeeding crop is less than when an equal amount of moderately rotted manure is employed, even when the two lots contain the same amount of available nitrogen. This difference is attributed to the much larger amount of energy at the disposal of the denitrifying bacteria in the fresh manure. The number of bacteria is of less importance. Considerable losses through denitrification will not take place in old, rotted manure; but denitrification does not entirely cease even when humification is far advanced.

The general conclusion is drawn that the value of dung as nitrogenous manure depends very essentially on the carbonaceous matter present; the use of plenty of peat litter in stables is recommended.

N. H. J. M.

Morphology and Biology of Denitrifying Bacteria. By HJALMAR JENSEN (*Bied. Centr.*, 1900, 29, 273—275; from *Centr. Bakt.*, 1898, 4, 401 and 448).—The term denitrifying bacteria is restricted to those which liberate free nitrogen; the bacteria which produce organic nitrogenous compounds, or nitrites and ammonia from nitrates, are not included.

The bacteria are aerobic in absence of nitrate, but utilise the oxygen of nitrate when present. Aeration prevents destruction of nitrates.

The bacteria at present known are: (1) *Bacillus denitrificans*, I., Burri and Stutzer = *Bacterium denitrificans*, Lehm. and Neum.; (2) *Bacillus denitrificans*, II., Burri and Stutzer = *Bacterium Stutzeri*, Lehm. and Neum.; (3) *B. Shirokikhi*, Jensen; (4) *B. denitrificans agilis*, Ampola and Garina; (5) *Vibrio denitrificans*, Sewerin; (6) *Bacillus pyocyaneus*, Sewerin; (7) *B. pyocyaneus*, Lehm. and Neum.

In addition to the above, the author has isolated four others: (8) *Bacterium filefaciens* (from an old cultivation of *B. Stutzeri*); (9) *B. centropunctatum* (from cow-dung and guinea-pig fæces); (10) *B. Hartlebii* (from soil from Ellenbach), and (11) *B. nitrovorum* (from horse-dung).

As regards the distribution of denitrifying bacteria, analyses of six samples of air gave negative results; it was, however, found that inoculation may take place through the air. Peat and autumn leaves of *Poa annua* and *Senecio vulgaris* gave negative results. Straw always gave positive results, and out of 17 samples of soil, 5 denitrified. In the soil, the bacteria are derived from the dung applied, and disappear if the soil is left unmanured. Fæces from cows, horses, and sheep frequently contained denitrifying bacteria; in the case of guinea-pigs, mice, pigs, and earth worms, the bacteria were sometimes found. Human fæces and the fæces of lions, dogs, canaries, and geese never contained the bacteria. The bacteria are destroyed in their passage through the human digestive system, and the same occurs with dogs and worms.

N. H. J. M.

Effect of Removing the Flowers on the Assimilation of Nitrogen by Leguminous Plants. By MARCO SOAVE (*Expt. Stat. Record*, 1900, 11, 516; from *Staz. sper. agrar. ital.*, 1899, 32, 499—516).—Comparing the results obtained when the flowers were constantly removed, with those obtained with similar plants which were left with the flowers, it was found that, in the case of *Vicia faba*, there was a decided gain in dry matter and nitrogen when the flowers were cut off. In the case of *Phaseolus multiflorus*, *Pisum sativum*, and *Lupinus albus*, there was a loss of either dry matter or nitrogen, or of both.

N. H. J. M.

Effect of Ferments on the Germination of Old Seed. By A. THOMSON (*Expt. Stat. Record*, 1899, 11, 460; from *Gartenflora*, 45, 344).—Cereal seeds, 20—25 years old, were soaked in diastase or pepsin solutions for 24 hours, washed and germinated. Barley which gave a germination of 4.5 per cent. germinated to the extent of 35 per cent. after treatment with 5 per cent. diastase solution, and 48 per cent. when a 10 per cent. diastase solution was employed; in a similar manner, the germination of oats was raised from 16 to 47 and 54 per cent. respectively. Pepsin (5 per cent. solution) increased the germination of the oats to 39 per cent. The germination of maize, peas, and clover rose from 3, 5, and 17 per cent. to 49, 22, and 50 per cent. when treated with 5 per cent. diastase solution.

N. H. J. M.

Relation of the Ash to the Height of Plants. By EDMUND J. MILLS, JOHN IMRIE, and ARCHIBALD GRAY (reprinted from *Proc. Phil. Soc. Glasgow*, 1900, 8 pp.).—The stem of a healthy spruce fir, cut down in December, was cut into 14 sections, each 19 $\frac{3}{8}$ inches long. These were burnt in a specially devised apparatus, described with sketch, and the weight of ash in each section determined; silica and lime were determined in the ashes. The actual weights of wood, ash, and constituents, as well as the percentage results, are given in tables, and the relations between the height of the tree and the weights of wood, ash, silica, and lime are shown in smoothed curves.

As regards silica, it was found that the point $h=3.1$ is a critical point, indicating the theoretical position at which the chemical effect of the unexposed trunk, as a mineral carrier, is at its lowest, owing probably to the sudden demand for ash by the large lowest branches. An upper critical point, $h=13.724$, was also found. This depends on the demand due to the exceptional vitality at the summit.

In the case of lime, the lower critical point is somewhat below that for silica; the higher critical point is of an ideal character, being above the top of the tree.

It is supposed that similar points occur in the branches, and even in the twigs.

N. H. J. M.

Distribution of Ash Constituents in the Section of the Copper Beech. By RICHARD HORNBERGER (*Bied. Centr.*, 1900, 29, 187—190; from *Mündener forstl. Hefte* 1898, 14. Compare *Abstr.*, 1897, ii, 280).—The intermediate portions of the sections of the two copper beeches previously examined (*loc. cit.*), corresponding with the 26th to the 87th and 90th years of growth, were divided into three portions, each

representing about 20 years of growth, for more detailed investigation. The middle portion (45th—65th years) was found to contain the least ash in the dry matter, the least phosphoric acid, and also the least, or, in the case of (B), almost the least, potassium; but it contained the greatest amount of calcium, and the most, or almost the most (in B), manganese.

In the same zone, but on different sides of the tree, there may be differences in the composition of the ash; even then, however, the results still show that potassium and phosphoric acid on the one hand, and calcium and manganese on the other, go together. N. H. J. M.

Composition of Cocoa-nut Ash. By A. BAIN and F. BACHOFEN (*Queensland Agric. Jour.*, 1900, 6, 297).—The different parts of the cocoa-nut weighed as follows: (1) Husk, 2·702; (2) shell, 0·546; (3) kernel, 0·875; and (4) milk, 0·593 lb., and contained (1) 34·44, (2) 84·80, and (3) 47·20 per cent. of dry matter, and 1·63, 0·29, 0·79, and 0·38 per cent. respectively of pure ash. Analyses of the ashes gave the following percentage results:

	K ₂ O.	Na ₂ O.	CaO.	MgO.	Fe ₂ O ₃ , Al ₂ O ₃ .	P ₂ O ₅ .	SO ₃ .	SiO ₂ .	Cl.
Husk ...	30·71	27·58	4·14	2·19	0·54	1·92	3·13	8·22	27·82
Shell ...	45·01	23·65	6·26	1·32	1·39	4·64	5·75	4·64	9·44
Kernel...	54·05	2·65	3·10	1·98	0·59	20·33	8·79	1·31	9·24
Milk....	34·54	13·95	7·43	3·97	trace	5·68	3·94	2·95	35·50

N. H. J. M.

Distribution of Sugar, Acid, and Tannin in Pears. By W. KELHOFER (*Bied. Centr.*, 1900, 29, 248—251; from *Jahresber. Wädensweil*, 6, 68). The following amounts of sugar (invert), acid (tartaric), and tannin were found in the different parts of the pear:

Skin.			Fruit.			Core.		
Sugar.	Acid.	Tannin.	Sugar.	Acid.	Tannin.	Sugar.	Acid.	Tannin.
7·74	6·20	2·80	8·24	14·83	2·36	7·31	11·71	0·97
Whole Pear.								
Sugar.	Acid.	Tannin.						
8·00	12·61	2·05						

Similar experiments were obtained with two other varieties of pears, (*Bied. Centr.*, 1899, 28, 68), and it is thought that it may be assumed that all varieties would show the same distribution of the different constituents at the same stage of ripeness. As ripening proceeds, the tannin diminishes more quickly in the inner parts of the pear than in the skin. By the time the pears had become doughy, the inside portions were free from tannin, whilst the skin still contained 1·9 per cent., or 65·8 per cent. of the original amount. The acid diminishes most quickly in the skin.

Analyses of three cross-sections of the pear, representing (1) the calyx, (2) the core, and (3) the stem portions, showed, after the removal of the calyx, &c., that the calyx portion contained the highest percentages of sugar, acid, and tannin. The seed portion contained the least tannin and the stalk portion the least sugar and acid. N. H. J. M.

Composition of the Albumens of the St. Ignatius Bean and Nux Vomica. By EMILE BOURQUELOT and J. LAURENT (*Compt. rend.*, 1900, 130, 1411—1413).—The albumen of the St. Ignatius bean when hydrolysed with dilute sulphuric acid yields 27 per cent. of mannose and 31 per cent. of galactose, and the albumen from nux vomica yields 11.3 per cent. of mannose and 41.6 per cent. of galactose. The carbohydrate of both albumens is therefore a mixture of mannan and galactan. Either of them can be used for the preparation of crystallised galactose, and will give a better yield than milk sugar. C. H. B.

Agaricus Campestris. By ALEXANDER ZEGA (*Chem. Zeit.*, 1900, 24, 285—286).—The mean result of various analyses give: Water, 89.22; nitrogen compounds, 5.94; fat, 0.23; nitrogen free material, 2.92; fibre, 0.84; and ash, 0.75 per cent. The ash contained P_2O_5 , 0.188; K_2O , 0.156; sand, 0.056. The finely-divided and air-dried fungus was extracted with alcohol at 45—50°, and in this liquid cholesterol and mannitol have been detected. J. J. S.

Composition of Apios Tuberosa. By CELSO BRIGHETTI (*Chem. Centr.*, 1900, i, 914—915; from *Staz. sperim. agrar. ital.*, 33, 72—75).—Analyses of the various portions of the plant, *Apios tuberosa*, are quoted. E. W. W.

Alinit in the Cultivation of Cereals. By L. MALPEAUX (*Ann. agron.*, 1900, 26, 196—211. Compare Abstr., 1899, ii, 242).—Inoculation with alinit had no effect on wheat grown in sand. When inoculated a second time in conjunction with applications of sugar and extract of straw respectively, the production of wheat was increased. Dung gave a greater increase than was obtained by inoculation, and the yield was further increased by inoculation in conjunction with dung. Alinit had a greater effect in increasing the production of wheat grown in rich soil, and the effect was increased by a second application of alinit, together with sugar. The increase due to inoculation was chiefly in the straw.

Field experiments were made with wheat and barley in soil containing 0.134 per cent. of total nitrogen. In the case of wheat, there was no increased production of grain after inoculation, but the straw was increased by about 300 kilos. In the barley experiment, the alinit plots gave slightly more grain and 410 kilos. more straw per hectare; with an application of sodium nitrate (150 kilos.), the yields of grain and straw were increased by 320 and 610 kilos.

The results showed, therefore, that inoculation with alinit is useless in absence of carbohydrates or a great deal of humus; in rich soil, it was decidedly beneficial, but sodium nitrate gave much the best results. Inoculation can only be of use when conditions favourable to the growth of the microbes exist in the soil; and Deherain has shown that, under these conditions, fixation of nitrogen can take place in soils without inoculation, which is, as a rule, superfluous. N. H. J. M.

[Composition of] Weak Straw. By J. ALAN MURRAY (*Ann. Rep on Field Expts. Univ. Coll. Wales*, 1899, 79—80).—Analyses were made of two lots of rye straw, (1) manured with phosphates, nitrogen, and potash; (2) with phosphates and nitrogen only. Whilst the more fully manured straw was in every respect normal, that obtained on the

plot which had no potash was too weak to stand, and when dried was so brittle that it could almost be reduced to powder when crushed in the hand. The air-dried straw from the two plots had the following percentage composition :

	Water.	Nitrogenous matter.	Oil.	Soluble carbohydrates.	Crude fibre.	Ash.
1.	10.29	6.11	3.35	46.01	30.64	3.60
2.	12.46	10.06	—	45.14	27.80	4.54

Both samples were cut when somewhat immature, but having been cut on the same day and grown from the same seed sown at the same time, the results are comparable.

When distilled with hydrochloric acid, the two samples yielded (1) 9.26 and (2) 10.95 per cent. of furfuraldehyde.

The results indicate that the weakness of the straw (2) cannot be due to defective lignification, and that it is probably connected with the deficient production of oil which was practically absent in the weak straw.

N. H. J. M.

Influence of Nitric and Ammoniacal Nitrogen on the Development of Maize. By PIERRE MAZÉ (*Ann. Inst. Pasteur.*, 1900, 14, 26—45. Compare Abstr., 1899, ii, 237, and Takabayashi, *ibid.*, 1897, ii, 585).—Maize plants grew equally well in solutions containing sodium nitrate and ammonium sulphate, provided that the strength of the latter solution did not exceed 0.05 per cent. ; stronger solutions are injurious. When both salts are present simultaneously, the plant sometimes prefers the one and sometimes the other. Ammonium salts are, therefore, not inferior to nitrate when employed in suitable quantities.

Reference is made to the Rothamsted experiments on wheat as regards the application of ammonium salts, the assumption being that nitrification is comparatively slow until June as indicated by Deherain's drainage experiments.* It is estimated that an application of 86 lbs. of nitrogen per acre would give a solution in the soil containing 0.075 per cent. of ammonium sulphate, and results are quoted indicating that this and larger amounts of ammonium salts are less beneficial than nitrate.

N. H. J. M.

Agricultural, Botanical, and Chemical Results of Experiments on the mixed Herbage of Permanent Grass-Land, Conducted for many Years in Succession on the Same Land. III. The Chemical Results. Section I. By SIR JOHN B. LAWES and SIR J. HENRY GILBERT (*Phil. Trans.*, 1900, B. 192, 139—210).—The experiments were commenced in 1856, and include about 20 plots, two unmanured and the rest with a variety of manures. The "agricultural results" and the "botanical results" obtained during the first 20 years of the experiments have already been

* The results of analyses of the drainage from the plots of the permanent wheat field at Rothamsted showed, however, that the nitrification of ammonium salts applied as manure to this soil is very rapid in October and November when the soil is sufficiently wet (compare Abstr., 1883, 891). In October, just after the ammonium salts have been applied, the drainage contains small amounts of ammonia, but if it is collected about a week or ten days later, it contains practically nothing but nitrates.—N. H. J. M.

discussed (*ibid.*, 1880, Pt. 1, and 1882, Pt. 4) and the present paper deals with the chemical results (determinations of total nitrogen, and ash analyses) of the same period.

The consideration of the results of the ash analyses showed the importance of including carbon dioxide in the "pure ash," instead of excluding it, as has almost invariably been done hitherto. The ash constituents are, therefore, calculated as percentages of the ash after saturation with ammonium carbonate and drying at 120—130°. The amounts of carbon dioxide in the ash ignited at a low red heat, and the amounts required to form normal salts, reckoning all the phosphoric acid as tribasic, are given in separate tables.

The ashes of different crops vary very characteristically according to the amount of nitrogen which they take up. For example, red clover, a crop which yields large amounts of nitrogen, partly due to fixation, much of which is taken up in the form of nitrates, yields an ash characterised by containing much carbon dioxide, which presumably represents organic acid originally present in the plant. The conclusion is drawn that, besides any physiological function of the bases, their role is prominently that of "carriers of nitric acid," and that, after the assimilation of the nitrogen, the base is left in combination with organic acids. It is suggested "that at any rate a large amount of the nitrogen of the chlorophyllous vegetation on the earth's surface was derived from nitrates; whilst, so far as this was the case, the *raison d'être* of much of the fixed base found in the ashes of plants would seem to be clearly indicated."

"The mineral composition of the mixed herbage is very directly dependent on the supplies available within the soil. Indeed, the composition of the mixed produce was found to be a somewhat close reflection of the supplies available within the range of the roots. It was, in fact, more so than in the case of individual crops grown separately. It is at the same time obvious, that when the more functionally important constituents are available in relative abundance, those which are of less importance in this respect are taken up and retained in less amount than they otherwise would be; the result being determined in great measure by the character of the growth induced.

"Luxuriance, or vegetative activity, is intimately associated with the amount of nitrogen available and taken up. Further, chlorophyll formation to a great extent follows nitrogen-assimilation. But the results relating to the increased amount of the non-nitrogenous substance yielded in the mixed herbage under the influence of various manures, clearly indicate that the nitrogen, being taken up, and the chlorophyll formed, the carbon-assimilation, and the carbohydrate formation, depend essentially on the amounts of potash available."

N. H. J. M.

Flax. By JULIUS OLSCHOWY (*Bied. Centr.*, 1900, 29, 240—242; from *Zeit. Landw. Versuchswesen Oesterr.*, 1899, 34, 135 and 515).—A crop of flax, 5000 kilos. per hectare, withdrew 34.1 kilos. of potash, 17.3 kilos. of nitrogen, and 15.5 kilos. of phosphoric acid from the soil. The assimilation goes on until the green seed capsules are formed, a period which represents about two-thirds of the whole vegetative period of flax grown for the production of fibre. Up to the time of flowering,

the assimilation of the above constituents is gradual; during the flowering period, there is a sudden increase followed by a rapid decrease.

Superphosphate, potassium sulphate, and sodium nitrate had a marked effect when applied before the seed was sown, but had no effect when applied as a top dressing. The effect of nitrogen was to increase the yield of straw and to lower the production of seed. Potash, and, still more, phosphoric acid, increased both straw and seed production.

N. H. J. M.

Effect of Nitragin and Inoculation Soil on Yellow Lupins. By MAX ADLER (*Expt. Stat. Record*, 1900, 11, 515; from *Ber. Landw. Versuchs Stat.* Jena, 1898, 19—20).—Lupins were grown in sandy soil in zinc pots; five without inoculation, five inoculated with nitragin, and five with inoculation from lupin soil.

Nitragin increased the corn and straw 34.4 and 12.2 per cent., whilst the increase after soil inoculation was, corn, 106.5, and straw, 42.9 per cent.

N. H. J. M.

Experiments with German, English, and French Varieties of Mangels. By FERDINAND WOHLTMANN (*Bied. Centr.*, 1900, 29, 242—247; from *Illust. Landw.-Zeit.*, 1899, Nos. 2 and 5).—The results of one year's experiments with 17 varieties of mangels, including the yields of roots and leaves, the weights of the roots, and the percentages of dry matter and sugar, are given. The results so far indicate that the best German varieties are hardly surpassed by any of the other varieties employed, but that greatest differences occurred in the yields of the German varieties.

N. H. J. M.

Sugar-Beet in 1898. By STONE, CLINTON, KINSELY, and CAVANAUGH (*Bied. Centr.*, 1900, 29, 254—256; from *Cornell Univ. Agric. Expt. Stat. Bul.*, 166, 1899).—Results obtained with eight varieties of sugar-beet are given.

Experiments on the effect of various manures, applied both alone and mixed, were made with Klein Wanzleben roots. Sodium nitrate alone greatly reduced the percentage of sugar and the purity coefficient.

N. H. J. M.

Mites in Beet-root Excrescences. By FR. BUBAK (*Zeit. Zuckerind. Böhm.*, 1900, 24, 355—367).—The excrescences sometimes observed on sugar-beet are produced by mites (*Histiostoma Feroniarum*, Duf.). The latter do not occur in healthy roots, and cannot exist in the excrescences in presence of microbes. The excrescences consist anatomically of the same substances as the roots, but the fibrovascular bundles are very irregularly placed. As regards composition, it has been shown by Schacht, Strohmer and Stift, and Stoklasa that the excrescences contain much less sugar than the roots, sometimes only half as much; whilst Strohmer and Stift and Bartoš found that the percentage of nitrogen is much higher than in the normal portions of the roots. It has been suggested that the less amount of sugar in the excrescences may be due to greater respiration, but it is more probably owing to consumption of sugar by the mites. Strohmer and Stift found 0.25—0.35 per cent. of invert sugar in the excrescences, but it is thought unlikely that it occurs in the healthy excrescences on roots

when taken up. When the excrescences are kept for a short time, the percentage of sucrose is reduced by 2—3 per cent.; subsequently, the sugar completely disappears.

N. H. J. M.

Rational Feeding of Cows. By OSKAR HAGEMANN (*Expt. Stat. Record*, 1899, 11, 484—485; from *Landw. Jahrb.*, 1899, 28, 485—534. Compare this vol., ii, 39 and 103).—Two cows were fed during successive periods with (1) malt sprouts, (2) pea-nut cake meal with cocoa-shells and molasses, (3) linseed meal, (4) maize-cake meal, (5) malt sprouts and 500 grams of emulsified sesamé oil, and (6) sesamé oil in a weak alkaline emulsion, in addition to a basal ration of hay, straw, dried beet diffusion residues, and salt.

The results gave no indication that the fat of food affects the production of milk fat. The milk of period 4 contained the least fat; the greatest yield of milk fat, as well as the highest percentage in the milk, was in the second period, when the ration contained 218 grams of fat for a cow weighing 560 kilos.

It is thought that the percentage of fat in milk and the absolute amount of milk fat produced do not depend on the fat digested in the food, but on certain substances present in some foods, which in some cases stimulate the lacteal glands, and in others modify the cell activity of the glands so as to produce milk containing more fat. This would account for the fact that cocoa-shells and molasses increased the fat in the milk, and that maize-cake maintained the yield, notwithstanding the natural shrinkage, although the percentage of fat in the milk diminished.

The substance which gives the characteristic sesame oil reaction was not transmitted to the milk.

N. H. J. M.

Feeding Experiments with Blood Molasses. By LILIENTHAL (*Bied. Centr.*, 1900, 29, 166; from *Landw. Presse*, 1899, No. 27).—Blood is preserved from decomposition by adding molasses, and blood molasses is now manufactured at all the large slaughter-houses in Germany. It may contain proteids, 17—19; fat, 2·3—3·5; and non-nitrogenous extract, 55—69 per cent.

Experiments in which horses received 4 lbs. of blood molasses in the place of 6 lbs. (out of 12 lbs.) of oats, gave satisfactory results. Good results were also obtained with cows which received 2 lbs. of blood molasses a day; the yield of milk was raised 2 litres a day, and the cows remained healthy. Further experiments will be necessary.

N. H. J. M.

Maize-germ Molasses as Food for Cows. By BERNHARD SCHULZE (*Bied. Centr.*, 1900, 29, 167—169; from *Fühling's Landw. Zeit.*, 1899, 524. Compare Abstr., 1899, ii, 448).—The food consists of 52·5 per cent. of molasses and 47·5 per cent. of maize-germs, and has the following percentage composition:

	Nitrogenous		Non-nitrogenous		
Water.	matter.	Fat.	extract.	Crude fibre.	Ash.
21·00	14·56	3·79	52·00	2·58	6·07

Feeding experiments with 6 cows were made, in which the cows received during four periods, besides hay (6 lbs.), clover hay (6 lbs.),

and sunflower cake (1 lb.), the following amounts of food: Periods 1 and 4, mangels (70 lbs.) and wheat husks (3 lbs.); period 2, mangels (62·5 lbs.), wheat husks (2 lbs.), and maize-germ molasses (2 lbs.); period 3, the same foods as (2) in amounts of 55, 1, and 4 lbs. respectively. The results showed that maize-germ molasses is exactly equivalent to mangels and wheat bran. N. H. J. M.

Feeding Cows with English Cake. By EBERHARD RAMM and E. MÖLLER (*Bied. Centr.*, 1900, 29, 234—235; from *Milchzeit.*, 1899, No. 18).—The cake consisted chiefly of cotton-seed meal, with a good deal of fibre and husks, and, in addition earth-nut, rice- and barley-husks, and small amounts of palm-kernel meal and molasses.

The results of feeding experiments showed that the cake had about the same value as earth-nut cake. The favourable results are attributed to the cotton-seed meal in conjunction with sugar. Owing, however, to the high percentage of crude fibre, the cake is not recommended. N. H. J. M.

Feeding Cows with Bassia-Nut and Palm-Bassia Cake. By EBERHARD RAMM and E. MÖLLER (*Bied. Centr.*, 1900, 29, 233—234; from *Milchzeit.*, 1899, No. 10, 15).—Bassia nuts are obtained from different varieties. The fat is used as food and for candles and soap, the residues being given to cattle. Bassia-cake contains: water, 8·75; proteids, 8·75; fat, 19·90; carbohydrates, 47·45; crude fibre, 9·75; and ash, 5·40 per cent.

The results of experiments with cows in which bassia-cake was compared with earth-nut cake showed that the two foods are very similar in value; the small amount of proteids is counter-balanced by the fat and carbohydrates, provided that the ration contains the necessary amount of proteids.

Similar results were obtained from cake resulting from the manufacture of oil from a mixture of palm-kernels (2 parts) and bassia-nuts (1 part); but it is thought preferable to utilise the two products separately. N. H. J. M.

Feeding Cows with Tropon. By EBERHARD RAMM and E. MÖLLER (*Bied. Centr.*, 1900, 29, 232—233; from *Milchzeit.*, 1899, No. 16).—The cows were fed with rations containing earth-nut cake and Finkler's tropon containing three times the normal amount of digestible proteid. The effect of the tropon was to increase the yield of milk by 0·216 kilo. and the dry matter free from fat by 0·04 kilo. The live weight was reduced by more than 1 per cent., and the percentages and yields of fat and dry matter in the milk were reduced. Tropon residues gave better results. N. H. J. M.

"Manur." By ALEXANDER ZEGA (*Chem. Zeit.*, 1900, 24, 264).—A cheese exported from Servia, prepared from the milk of cows or sheep. The milk is brought to the boiling point and when cold a mixture of butter milk, whey, and a specially prepared rennet is added. The cheese paste is pressed in cloth, slightly salted, and dried. Its composition is about as follows: water, 22·40—23·13; proteids, 17·35—16·80; fat, 52·86—51·22; carbohydrates, 3·41—4·32;

ash, 4.48—4.53; salt, 3.26—3.40. Calculated on the dry substance: proteids, 22.35—21.80; fat, 68.11—66.63 per cent.

It has no particular odour, tastes sweetish, and when cut leaves a perfectly smooth surface.

L. DE K.

Soil Analyses. By CARL VON FEILITZEN (*Bied. Centr.*, 1900, 29, 217—218; from *Svensk. mosskulturfören. tidskr.*, 1899, 271—282).—Determinations of total nitrogen, and of potash, lime, and phosphoric acid, dissolved by 12 per cent. hydrochloric acid, were made in several hundred samples of soils from the different provinces of Sweden. Forty-five per cent. of the samples contained more than 8000 kilos. of nitrogen per hectare, to a depth of 20 cm., and 33 per cent. less than 6000 kilos.; 13 per cent. contained more than 600 kilos. of phosphoric acid and 74 per cent. less than 400 kilos.; whilst as regards lime, 50 per cent. contained more than 4000 kilos., and 39 per cent. less than 3000 kilos. per hectare. The peat-land of Gothland was particularly rich in lime, 96 per cent. of the samples containing over 4000 kilos. per hectare.

N. H. J. M.

Effect of Carbon Disulphide on the Fertility of Arable Soil. By EWALD WOLLNY (*Bied. Centr.*, 1900, 29, 146—150; from *Vierteljahrsschr. Bay. Landw.-rats.*, 1898, 319. Compare Oberlin, Abstr., 1896, ii, 67, and Pagnoul, *ibid.*, 66).—The results of pot and field experiments showed that whilst the application of carbon disulphide to soil will destroy the vegetation more or less completely, the fertility of soil is generally considerably increased when the disulphide is applied some months before sowing the seed. The increased fertility, which cannot at present be explained, lasts over one or several vegetative periods and is followed, if no manure is applied, by a considerable falling off.

Nitrifying and other soil microbes, including the leguminous nodule-bacteria, are not destroyed by even large amounts of carbon disulphide; their activity is only temporarily suspended.

N. H. J. M.

Experiments on the Schultz-Lupitz System. By PAUL BASSLER (*Bied. Centr.*, 1900, 29, 154—157; from *Ber. Agr.-Chem. Versuchs u. Samenkontrol-Station Köslin* for 1897, 81).—Field experiments were made on various light and other soils to ascertain whether liming or marling, in conjunction with moderate amounts of mineral manures and green manuring with *Leguminosæ*, would give, under the unfavourable climatic conditions of the Eastern provinces, results similar to those obtained by Schultz-Lupitz. The composition of the soils is given in each case; about half of them contained satisfactory amounts of phosphoric acid, but all were poor in lime, and some contained very little potash. Several of the experiments failed owing to unfavourable weather.

The potato crop of 1897, which was injured by drought, was scarcely benefited by minerals on the fields which had green manure. On one field, the crop was better after the ploughing in of serradella, containing 156.5 kilos. of nitrogen per hectare, than after lucerne containing 322 kilos. of nitrogen. The loosening of the subsoil raised,

in nearly every case, the percentage of starch (about 0.3 per cent.) in the tubers, and in the majority of cases also increased the crop.

N. H. J. M.

Composition of the Soil under Paved and other Manure Courts at different Depths. By ADOLF EMMERLING and H. WEHNERT (*Bied. Centr.*, 1900, 29, 157—158; from *Jahresber. Versuchs Stat. Kiel.*, 1898, 23).—The conclusion is drawn that to ascertain the extent of the losses undergone by a manure heap, it is better to examine the drainage collected in a pit, than to analyse the different layers of soil; no analytical results are therefore given.

N. H. J. M.

Manurial Experiments on Irrigated Meadows. By MARIO ZECCHINI and R. NUOLI (*Bied. Centr.*, 1900, 29, 159—162; from *Staz. sper. agrar. ital.*, 1899, 32, 15).—Farmyard manure gave the greatest yield of hay. Mineral and bone superphosphate proved to be about equal in value, and no difference in value was found between sodium nitrate and ammonium sulphate.

N. H. J. M.

Nitragin. By D. DICKSON and L. MALPEAUX (*Jour. agr. prat.*, 1897, 61, i, 191—197).—Inoculation of soil on which leguminous plants had not been grown previously, increased the yields of vetches and white lupins from 113 and 226 grams to 152 and 282 grams respectively. In sand, inoculation with nitragin increased the yields of incarnate clover and white lupins from 111 and 204 grams to 167 and 250 grams.

The results of field experiments with the same plants showed that inoculation had very little effect. In both sets of experiments, application of nitragin to the soil gave better results than when the seed was inoculated. The percentage of nitragin in the produce was increased by inoculation. The composition of the clover and lupins, both inoculated and grown without inoculation, is given.

N. H. J. M.

Nitragin. By E. SCHRIEBAUX (*Jour. agr. prat.*, 1897, 61, i, 813—819).—Pot experiments were made in which clover and peas respectively were grown in sterilised sand both without and with addition of nitragin. In the case of clover, inoculation with clover-nitragin greatly increased the growth, whilst inoculation with pea-nitragin produced no nodules and had no beneficial effect on the growth. With peas, both pea- and clover-nitragin produced nodules; with pea-nitragin, the produce was increased by about 50 per cent., whilst clover-nitragin reduced the yield.

Experiments with clover grown in soil showed that nitragin had no effect; the soil already contained the microbes.

N. H. J. M.

Importance of Various Plants employed for Green-manuring, in Increasing the Amount of Nitrogen in the Soil. By H. C. LARSEN (*Bied. Centr.*, 1900, 29, 230—232; from *Tidsskr. Landbr. Plantæavl.*, 1899, 5, 101—112).—Several kinds of plants were grown in pots containing 7 kilos. of light soil (N = 7.03 grams per pot) with mineral manures. The non-leguminous plants, especially buckwheat, and some leguminous plants (vetches) left the

soil poorer in nitrogen, whilst the other *Leguminosæ* either had no effect on the amount of nitrogen in the soil, or else increased it.

As regards total nitrogen, the nitrogen of the soil, roots, and above-ground portions of the plants, there was a gain in every case with the *Leguminosæ*, the greatest gains being obtained with *Vicia sativa narbonneensis*, *Pisum arvense*, and *Melilotus albus*.

The portions of the plants left after taking samples were mixed with the soil, and left during the winter. Experiments with barley showed that manuring with buckwheat and mustard was not only much less effective than manuring with leguminous plants, but that less growth was obtained than without green manure. N. H. J. M.

Effect of Manuring on the Inner Processes of some Plants. By HERMANN MÜLLER (*Bied. Centr.*, 1900, 29, 225—226; from 7th *Jahresber. Wädenswil.*, 36).—Potatoes, celery, radishes, and carrots were manured with minerals with 10 and 30 grams respectively of sodium nitrate per square metre in addition; one bed in each case received minerals only. The effect of nitrate was soon very marked, especially in the case of celery. The yield from each bed is given. Increased yields were obtained in each case, except potatoes and carrots, under the influence of nitrate. The radishes on the nitrate beds were partly decayed; the average weight was, however, considerably increased by the larger amount of nitrate. The carrots were also in part decayed on the nitrate beds. The potatoes, however, did not decay, and the diminished yield is attributed to the formation of crusts on the surface of the soil, due to the nitrate. N. H. J. M.

Availability of Fertiliser-Nitrogen. By SAMUEL W. JOHNSON, EDWARD H. JENKINS, and W. E. BRITTON (*Ann. Rep. Conn. Agric. Expt. Stat.*, No. 21, for 1897. Compare this vol., ii, p. 42).—Oats were grown in pots containing soil from the maize field, to which the various manures were added. The following results show the availability of the different forms of nitrogen for oats: sodium nitrate, 100; dried blood, 73·3; dry ground fish, 63·9; ground bone, 16·7; tankage, 49·4; horn and hoof, 68·3; linseed meal, 68·9; cotton seed meal, 6·48; and castor pomace, 64·6. If the roots were to be excluded, the percentage availability would have to be reduced by about 12; even then, greater amounts, especially in the case of nitrate and dried blood, will be seen to have been assimilated in 1897 than in the previous experiments. In the experiment next described, Hungarian grass was grown in soil to which nitrate, cotton seed meal, and raw knuckle bone, free from tendon and grease, were added. The bone was in three degrees of fineness: (A) passed through holes $\frac{1}{1\frac{1}{2}0}$ inch in diameter; (B) through holes $\frac{1}{50}$ to $\frac{1}{1\frac{1}{2}0}$ inch; and (C) through holes $\frac{1}{25}$ to $\frac{1}{50}$ inch; the three grades contained 3·58, 3·88, and 4·08 per cent. of nitrogen. The nitrogen availability was as follows: sodium nitrate, 100; cotton seed meal, 57·9; bone (A) 11·5, (B) 8·5, and (C) 5·6. N. H. J. M.

Phosphates. By CONSTANT SCHREIBER (*Bied. Centr.*, 1900, 29, 162—164; from *Rev. gén. agron.* Compare *ibid.*, 1897, 26, 803).—Phosphorite and basic slag had no effect on the growth of lupins and

white beans owing, it is supposed, to the power possessed by these plants, as well as by vetches, of obtaining all the phosphoric acid they require from the soil. Mineral phosphates should not be applied for cereals, tobacco, flax, carrots, sugar-beet, potatoes, and maize, and it is not worth while to apply them to serradella, and incarnate, red and white clover. Mineral phosphates are, however, of use in the case of hemp, the *Cruciferae*, peas, vetches (?), and buckwheat.

As regards the use of mineral phosphates in different soils, it was found that results are only certain in the case of peat-land.

In experiments with peas, it was found that calcium carbonate was in every case injurious when mineral phosphates were employed, and that when the amount of carbonate was large, its effect extended to the next year. Similar results were obtained with mustard and with clover, when phosphoric acid was applied in the form of mineral phosphate; in conjunction with basic slag, however, calcium carbonate had practically no injurious effect.

N. H. J. M.

Basic Slag for Spring Manuring. By PAUL WAGNER (*Bied. Centr.*, 1900, 29, 218—220; from *Deut. landw. Presse*, 1895 [?], No. 21, 183).—Basic slag containing 85—95 per cent. of phosphoric acid, soluble in citric acid, can be applied at all times, and will at once be available. The whole principle of phosphate manuring consists in applying an excess of the manure until a further addition produces no effect; in subsequent years, just sufficient phosphate is applied to meet the requirements of the greatest possible crop. The phosphoric acid does not become unavailable. A meadow which only yielded 30 cwt. of hay per hectare was partly manured, in 1899, with basic slag (16 cwt. per hectare); the whole meadow received kainite (16 cwt. per hectare) at the same time (1889) and in each subsequent year. The effect of the one application of basic slag was to increase the yield of hay, not only in 1890, but in each subsequent year as well, the total increase (1890 to 1896) being 243 cwt. per hectare. The greatest increase was in 1894 (59 kilos.), five years after the manure was applied. N. H. J. M.

Composition of Kraal Manure. By J. LEWIS (*Agr. Jour. Cape of Good Hope*, 1899, 15, 517—521).—Analyses of (1) eleven samples of sheep-dung deposits, and of (2) three samples of burnt kraal manure are given. The average composition of the air-dried substances are as follows:

	Water.	N.	Ash.	K ₂ O.	CaO.	P ₂ O ₅ .	Cl.
(1)	13.52	1.31	41.28	2.84	7.08	1.26	1.25
(2)	2.23		86.46	7.60	16.97	2.59	1.57

N. H. J. M.

Analytical Chemistry.

Acidimetry. By A. ASTRUC (*Compt. rend.*, 1900, 130, 1563—1564. Compare Abstr., 1898, i, 222; and this vol., i, 199; ii, 122).—*iso*-Ethionic acid behaves as a strong monobasic acid in the presence of phenolphthalein, litmus, rosolic acid, and Poirrier's blue. With methyl-orange, 0.95 mol. of the alkali is required to give the end point.

Sulphanilic acid may be titrated with the above indicators, including methyl-orange, in this respect differing from the aminobenzoic acids.

Meconic acid behaves as a dibasic acid towards all the indicators except Poirrier's blue; with this reagent, it exhibits a tribasic character.

Mellitic acid reacts as a tribasic acid towards methyl-orange; its hexabasicity is revealed by the use of the other indicators.

G. T. M.

Asbestos Filters. By OTTO LOHSE and P. THOMASCHESKI (*Zeit. anal. Chem.*, 1900, 39, 158—161).—To furnish proof of the utility of Lohse's pattern of asbestos filters (Abstr., 1899, ii, 801), the authors have made numerous estimations of silver, chlorine, barium, sugar (by copper reduction), and nickel, with results which showed only small differences in the fourth significant figure. When the precipitate is to be heated in a current of gas, it may be collected on a layer of coarse crushed glass (2—4 mm.) above the asbestos plug. M. J. S.

Technical Gas Analysis. By C. SCHMIDT (*Chem. Centr.*, 1900, i, 923; from *J. Gasbel.*, 43, 231—232).—In the technical analysis of gases over water, after absorbing the carbon dioxide, heavy hydrocarbons, oxygen, and carbon monoxide, a residual gas is obtained consisting of hydrogen, methane, and nitrogen.

In order to analyse this with a sufficient degree of accuracy, 20 c.c. of the mixture are measured in a Bunte burette, mixed with 125 c.c. of air, and exploded. After absorption of the carbon dioxide formed in the explosion, the total contraction is read off, and the remaining free oxygen, which should occupy about 2—5 c.c., is estimated by absorption with phosphorus. The remainder consists of nitrogen, from which should be deducted the amount of nitrogen contained in the added air (air \times 0.791).

The following formulæ should be used:

$$H = \frac{4}{3} (K + C) - 2V_0 \quad CH_4 = V_0 - \frac{1}{3} (K + C),$$

in which V_0 is the oxygen consumed, C the contraction, and K the generated carbon dioxide.

L. DE K.

Estimation of Combined Hydrochloric Acid in Gastric Juice. By OTTO COHNHEIM and H. KRIEGER (*Chem. Centr.*, 1900, i, 996; from *Münch. med. Wochschr.*, 47, 381—382).—The authors estimate in the ordinary manner the joint acidity and the free acid, each in 10 c.c., of the filtered gastric juice; 10 c.c. are then precipitated with calcium phosphotungstate. (This solution is made by

preparing a 4 per cent. solution of commercially pure phosphotungstic acid, and neutralising this at the boiling point with calcium carbonate; the solution keeps, and 30 c.c. will always be sufficient.) The bulky precipitate is filtered off, and the acidity estimated in the filtrate, using rosolic acid or phenolphthalein as indicator; the difference between this and the total acidity represents the combined hydrochloric acid. If there should be a deficiency of free hydrochloric acid, the deficit is estimated in the usual way, and a known volume of standard hydrochloric acid, about 30—40 c.c. more than the deficit amounts to, is added; the amount of the deficit is to be deducted from the amount of combined acid found.

L. DE K.

Estimation of Chlorine in Gastric Juice. By G. MEILLERE (*Bull. Soc. Chim.*, 1900, [iii], 23, 404—405).—The chlorine existing as free hydrogen chloride is estimated by titration with standard baryta solution, using phenolphthalein as indicator. The total chlorine is determined in the solution obtained by evaporating the juice to dryness with excess of calcium carbonate and calcium nitrate, igniting at a low temperature, and extracting the residue with dilute acetic acid. It is useful also to estimate the chlorine in the residue obtained by evaporating the juice to dryness in a vacuum, and in the ash.

N. L.

Chemical Processes in the Stomach. By M. C. SCHUYTEN (*Chem. Zeit.*, 1900, 24, 234—235).—The author has investigated the behaviour of the following reagents, which are usually recommended in testing for minute quantities of hydrochloric acid, towards the more common organic acids: (1) Danilewsky's reagent (Tropæolin OO); (2) Boas's reagent (a mixture of resorcinol and sugar in aqueous or alcoholic solution); (3) Günzburg's reagent (a mixture of phloroglucinol and vanillin in alcoholic solution); (4) an alcoholic solution of Congo red. The conclusion arrived at is that, to prove the presence of free hydrochloric acid in the juices of the stomach, freshly prepared Boas's reagent must be employed, as this reagent is not affected by small quantities of free organic acids, with the exception of tartaric acid, whereas most of the other reagents mentioned are readily affected.

Further experiments have proved that neither carbon dioxide nor different types of fatty acids are capable of liberating free hydrochloric acid from sodium or potassium chloride by their mass action (compare Maly, *Zeit. physiol. Chem.*, 1877, 1, 74).

J. J. S.

Estimation of Ozone from Ozonisers of Large Dimensions. By EUG. ACKERMANN (*Chem. Zeit.*, 1900, 24, 235—236).—A criticism of the method now in vogue of passing a definite volume of ozonised air through a solution of potassium iodide acidified with sulphuric, hydrochloric, tartaric, or other acid, and titrating the liberated iodine.

The method gives very uncertain results, owing to the great technical difficulty of accurately measuring the volume of gas which passes through the iodide solution.

L. DE K.

An Addition to the Apparatus for Kjeldahl's Nitrogen Estimation. By H. MEHRING (*Zeit. anal. Chem.*, 1900, 39, 162—163).

In place of the bulb-tubes of various forms usually inserted between

the flask and condenser to arrest drops of the alkaline liquid, a wide tube, twice bent at obtuse angles in opposite directions, and with narrow ends for making the respective connections, is employed. In the straight, narrow, vertical tube connected with the flask, a column of condensed liquid, about 10 cm. high, collects, and washes the ascending vapour; the upper, narrow tube is bent to a swan-neck shape. Owing to its simplicity, the apparatus is but little liable to fracture, and excellent results are obtained by its use. M. J. S.

Estimation of Nitrous Acid. By GYSBERT ROMIJN (*Chem. Zeit.*, 1900, 24, 145—146).—A criticism of Erdmann's view regarding the importance of nitrous acid in water, and of his patented new reagent (a liquid, containing sodium sulphanilate and hydrochloric acid, and a powder, a mixture of sodium 1-amino-8-hydroxynaphthalene-4:6-disulphonate with sodium sulphate; this vol., ii, 243).

The results obtained with this new reagent were less satisfactory than those got with Griess' reagent. L. DE K.

Estimation of the Phosphoric Acid available as Plant Food in Soils and Manures. By J. PLOT (*Chem. Centr.*, 1900, i, 996—997; from *Oesterr. Chem. Zeit.*, 3, 127—131).—In order to ascertain the available phosphoric acid in soils or manures, a solvent should be used which resembles as much as possible the juice contained in the root of the plant. The author has now prepared a solvent which is a close imitation of the juice of beet in respect to salts. 0.4004 gram of ferrous sulphate, 1.4616 grams of potassium sulphate, 3.7098 grams of calcium nitrate, and 2.890 grams of magnesium chloride are dissolved and made up to 1 litre. 7.0566 grams of crystallised sodium carbonate, 6.744 grams of potassium carbonate, and 0.2 gram of silicic acid are fused in a platinum crucible; the fused mass is dissolved in water and mixed with 2.75 grams of oxalic acid, 1.9840 grams of malic acid, 2.2994 grams of citric acid, 1.9396 grams of tartaric acid, and then diluted to 1 litre. Before use, equal parts of these solutions are mixed.

25 grams of air-dried soil, or 5 grams of a manure, are shaken for half an hour in a 500 c.c. flask filled with the liquid; the phosphoric acid is then estimated in 200 c.c. of the clear filtrate. The process is well adapted for soils. When dealing with manures, it must be remembered that their soluble phosphoric acid available as plant food may be reduced in quantity when applied to a particular soil. The true value of a manure is, therefore, best ascertained by first analysing the soil itself, and then another portion mixed with a definite amount of the manure. L. DE K.

Sodium Amyl-xanthate in Qualitative Analysis. By R. GRASSINI (*Chem. Centr.*, 1900, i, 922—923; from *L'Orosi*, 22, 369—372).—The author has used Papasogli's reagent (*ibid.*, 21, 265) (which consists of a yellow solution prepared by mixing equal volumes of 50 per cent. solution of sodium hydroxide, pure amyl alcohol, and carbon disulphide) for other metals beside nickel and cobalt, and has observed the following colour reactions: Silver in ammoniacal solution turns dark blood-red with 2—3 drops of the reagent; lead, in neutral

solution, gives an orange precipitate soluble in sodium hydroxide; mercurous salts give a brownish-black, mercuric salts a dirty yellow, antimony in hydrochloric acid solution (acid solutions require some more of the reagent) an orange, arsenic in acid solution a canary-yellow, tin in acid solution a brown, bismuth in acid solution a reddish-brown, cadmium in ammoniacal solution a bright yellow precipitate; copper in very dilute ammoniacal solution is coloured red, aluminium dissolved in a not too dilute solution of sodium carbonate (1 hydroxide) gives a white, gelatinous precipitate; iron, in a neutral or faintly acid solution, turns a deep yellowish-red; manganese behaves like iron, but the red colour is not so permanent. Chromium, zinc, calcium, barium, strontium, magnesium, potassium, and sodium gave no reaction.

The reagent is, therefore, useful for the identification of individual metals from the groups previously separated from each other by the usual methods.

L. DE K.

Direct Estimation of Calcium in Presence of Iron and Aluminium. By L. BLUM (*Zeit. anal. Chem.*, 1900, 39, 152—155).—In the estimation of calcium in iron ores and blast furnace slags, an important economy of time results from precipitating the calcium by ammonium oxalate from a solution which has not been freed from iron and aluminium, but in which the oxides of those metals are retained in ammoniacal solution by the presence of tartaric acid. For practical purposes, the results of the two methods agree closely, since the amount of the iron, aluminium, and manganese oxides precipitated with the calcium from the ammoniacal tartrate solution is almost exactly balanced by the calcium oxide which escapes precipitation. The method is confined, however, to substances containing less than 0.5 per cent. of manganese.

M. J. S.

Analysis of Calcium Carbide. By HUGO ERDMANN and M. VON UNRUH (*J. pr. Chem.*, 1900, [ii], 61, 233—236).—An apparatus is described in which a known weight of a sample of calcium carbide is allowed to fall into water; the gas evolved escapes after passing over soda lime and from the loss in weight of the apparatus the proportion of calcium carbide in the sample is calculated. The amount of acid required to neutralise the resulting calcium hydroxide is calculated and subtracted from the actual amount required, thus giving the proportion of lime present in the sample. The neutral insoluble residue is also filtered off and estimated.

R. H. P.

Evaluation of Commercial Calcium Carbide. By GAETANO MAGNANINI and F. VANNINI (*Gazzetta*, 1900, 30, i, 401—404).—A description is given of a simple apparatus for determining the volume of acetylene yielded by a given weight of calcium carbide.

T. H. P.

Volumetric Estimation of Mercuric Chloride in Dressings. By MARTIN LEHMANN (*Chem. Centr.*, 1900, i, 998—999; from *Pharm. Zig.*, 45, 238—239).—The author communicates a further process for the volumetric estimation of mercuric chloride (this vol., ii, 443). It is based on the action of phosphorous acid on mercuric chloride which yields mercurous chloride and phosphoric acid. The excess of phos-

phorous acid is then titrated with *N*/100 potassium permanganate or with *N*/100 iodine, using starch as indicator. The action of the phosphorous acid is complete within half an hour at 25–30°. As the solution does not keep, it must always be checked afresh.

If the dressings should be coloured by rosaniline, this may be removed by means of a little animal charcoal. Experiments to estimate the mercuric chloride by means of standard stannous chloride or by *N*/100 potassium ferrocyanide and potassium permanganate have failed to give accurate results.

L. DE K.

Dry Assay of Lead. By J. FLATH (*Chem. Zeit.*, 1900, 24, 263–264).—A series of experiments to show that the dry assay is quite accurate enough for technical purposes; in rich ores, the deficiency does not exceed 1.5 per cent., and it must be remembered that some accompanying metals such as copper and antimony partly pass into the lead regulus.

The most suitable composition of the flux intended either for an acid or a basic material is sodium carbonate, 70 parts; borax, 28 parts; and potassium hydrogen tartrate, 2 parts.

L. DE K.

Estimation of Iron in Tap Cinder. By L. BLUM (*Zeit. anal. Chem.*, 1900, 39, 156–157).—In consequence of the almost universal presence of vanadium in the slag from iron puddling, neither the permanganate nor the stannous chloride volumetric method is available for an exact estimation of the iron. The gravimetric method is the only trustworthy one. The hydrochloric acid solution of the substance (freed from silica) should be twice precipitated by boiling with ammonium acetate to eliminate manganese; the precipitate again dissolved in hydrochloric acid, and, after adding tartaric acid and excess of ammonia, ammonium sulphide added to precipitate the iron.

M. J. S.

Simple Method for Decomposing Chrome-iron Ore. By RUDOLF FIEBER (*Chem. Zeit.*, 1900, 24, 333).—0.5 gram of the finely powdered ore is fused in a platinum crucible with 3 grams of sodium potassium carbonate for 10 minutes; when cold, 3 grams of dry borax are added and the mixture is again fused by first heating for a short time over the flame of a Teclu burner, and then for 45 minutes over the blowpipe. If the decomposition is not yet complete, a further addition of sodium potassium carbonate should be made. It is not really necessary to use the blast; if time is no object, a prolonged heating over the flame of a large Teclu burner will answer the purpose.

L. DE K.

Tin in Preserved Meat; Its Estimation and the State in which it Occurs. By F. WIRTHLE (*Chem. Zeit.*, 1900, 24, 263).—Analyses are communicated of samples of tinned meat from 1 to 5 years old, and the percentage of tin is stated. Where the metal was found to be corroded, which nearly always had occurred at such spots as had been in contact with the fat, the cause of the corrosion was found to be due to the formation of basic stannous chloride. The following process, originated by Orfila, was used for the estimation of the tin.

120 grams of the meat (jelly, fat) are heated in a large porcelain

dish standing on an asbestos plate with 5 c.c. of strong sulphuric acid with constant stirring, adding gradually more sulphuric acid; in all about 15—20 c.c. In this way, after about 4—5 hours a porous, charred mass is obtained which is then powdered and burnt to ash in a porcelain crucible. The ash is now fused with a mixture of sodium nitrate and carbonate, the fused mass treated with water and saturated with carbon dioxide. After remaining overnight, the precipitate is collected, washed, dried, and fused in a covered crucible with potassium cyanide. The fused mass is dissolved in water, the insoluble matter collected, washed, and dissolved in hydrochloric acid. From this solution, the tin is then precipitated in the usual manner with hydrogen sulphide and weighed as oxide. To make sure, this may be fused again with potassium cyanide and once more precipitated with hydrogen sulphide.

L. DE K.

Tinned Fish. By ADELBERT RÖSSING (*Zeit. anal. Chem.*, 1900, 39, 147—152).—The examination of some tins in which sterilised cod-fish and lobsters had been preserved for some years showed that the metal had been strongly attacked and in some cases completely removed from the interior, being converted into a white crust containing stannic oxide, phosphoric acid, and iron. This effect seems to be due to the action of the phosphates and ammonia present. It is in no way connected with imperfect sterilisation, but may always be regarded as evidence of long keeping. Any putrefication or alteration in the original fresh appearance of the contents of the tins is not to be ascribed to this chemical action on the metal (except in cases where the iron itself is strongly attacked), but is the result of want of cleanliness or of sufficient rapidity in the operation of tinning, or of insufficient sterilisation of the contents of the tin.

M. J. S.

A New Reagent for Phenolic Compounds. By G. CANDUSSIO (*Chem. Zeit.*, 1900, 24, 299—301).—Instead of ferric chloride as a general test for phenols, the author uses a 1 per cent. solution of potassium ferricyanide to which 10—20 per cent. of pure ammonia has been added. This solution has the advantage over ferric chloride that it may be applied to either acid or alkaline solutions. The test may be applied in three ways. (1) By adding the reagent drop by drop to the phenol. (2) By adding the phenol gradually to an excess of the reagent. (3) By adding the reagent drop by drop to a solution of phenol rendered alkaline with sodium hydroxide. The results are communicated in a lengthy table.

From this, it is shown (1) that the sensitiveness of the ferric chloride test and the new test is in some cases the same, but in other cases different, the iron test being generally the less sensitive; (2) that although the phenolic compounds give with ferric chloride a blue, and with potassium ferricyanide mostly a brown colour, there is generally produced a series of different colours or precipitates which are of practical importance; (3) that potassium ferricyanide gives with phenol and commercial guaiacol a brown, with β -naphthol a vermilion, with thymol and morphine a whitish-yellow, with synthetical guaiacol a flesh-coloured, and with eugenol a yellow precipitate; (4) that potassium ferricyanide gives with α -naphthol a

single colour, namely, a blackish-violet, whilst it also gives a single colour with sodium salicylate, vanillin, morphine, and phloroglucinol, namely, a yellow one; (5) that, on the other hand, phenol, guaiacol, creosote, resorcinol, orcinol, catechol, quinol, gallic acid, pyrogallol, and tannic acid give with the same reagent two or more colours in succession. The sensitiveness of the two reagents towards artificial guaiacol, commercial guaiacol, and creosote is remarkable, as it gradually decreases from the first to the third.

It is also worthy of notice that thymol gives with ferric chloride a precipitate soluble in alcohol, and with potassium ferricyanide a precipitate insoluble in that liquid, whilst eugenol behaves in the opposite way. Morphine, like thymol, also gives a precipitate with potassium ferricyanide insoluble in alcohol.

L. DE K.

Detection of Sucrose in Lactose. By JOHN LANDIN (*Chem. Zeit.*, 1900, 24, 211).—The sample is treated with strong sulphuric acid. If the lactose is pure, it turns pale yellow at first and then gradually becomes bright brownish-red, the acid itself showing a red-dish colour. If, however, a small quantity of sucrose is present, the mixture assumes at once a dark colour and soon becomes dark brown or brownish-black, and the acid does the same. In the presence of much sucrose, the whole mass turns black at once.

If a quantitative estimation is required, this may be effected by taking the copper reducing power before and after inversion.

L. DE K.

Volumetric Estimation of Free Fatty Acids. By J. SWOBODA (*Chem. Zeit.*, 1900, 24, 285).—A standard solution of sodium hydroxide in alcohol is very unstable, whilst an aqueous solution may cause the precipitation of fatty matter, which must then be redissolved by warming. If the liquid to be titrated contains ether as well as alcohol, two layers are formed which necessitate vigorous shaking after each addition of the alkali.

These inconveniences are avoided by dissolving the fatty matter in a mixture of 1 part of absolute alcohol and 2 parts of amyl alcohol.

L. DE K.

Estimation of Salicylic Acid. By JOSEF MESSINGER (*J. pr. Chem.*, 1900, [ii], 61, 237—248. Compare W. Fresenius and L. Grünhut, *Abstr.*, 1899, ii, 580).—The author shows that the iodometric method of estimating salicylic acid described by him and Vortmann (*Abstr.*, 1890, 1473), but rejected by Fresenius and Grünhut (*loc. cit.*), is quite satisfactory if the iodine and sodium hydroxide are present in sufficient quantity. The process is also satisfactory for other phenols.

R. H. P.

Hübl's Iodine-addition Method. By PAUL WELMANS (*Chem. Centr.*, 1900, i, 926—927; from *Zeit. öffentl. Chem.*, 6, 86—96).—The author's object has been to prepare an iodine solution of great stability, and he now recommends the following liquid for determining the iodine number of fats: 30 grams of iodine, 30 grams of powdered mercuric chloride, and 500 grams of glacial acetic acid are put into a litre flask, and ethyl acetate is then added, leaving space sufficient for

the mixture to be effectively shaken. When solution is complete, the liquid is made up to a litre by adding more ethyl acetate. This solution being an excellent solvent for fats, the use of chloroform becomes superfluous.

A number of analyses are communicated showing the influence of time, temperature, and excess of iodine on the iodine number. With lard, the excess of iodine is of more influence than the time of action; with cotton-seed oil and oil of almonds, no difference is noticed. With castor oil, the results are influenced by the time of action; various kinds of poppy oil behave differently in that respect. With cod-liver oil, the results vary, first with the temperature, then with the time of action, and lastly with the excess of iodine.

The fat extracted from roasted cocoa or chocolate by means of ether, unless dried for several hours at 105°, shows far too high an iodine number. This is caused by the presence of acraldehyde, which may, however, be removed by washing the fat with water at 50°.

L. DE K.

Estimation of Urea in Urine. By ADOLF JOLLES (*Zeit. anal. Chem.*, 1900, 39, 137—145).—The methods of Knop, Hufner, and Riegler are recognised as giving results in excess of the truth; the author finds that the methods of Pflüger (*Abstr.*, 1887, 90) and Freund and Töpfer (*Wein. Klin. Rundschau*, 1899, 371) give practically identical results, and the latter estimates correctly any artificial addition of urea to urine. In both methods, the use of the azotometer replaces advantageously the estimation of the nitrogen by Kjeldahl's process, and these methods may be further improved as follows:

Freund and Töpfer's Method.—Five c.c. of the urine mixed with 5 c.c. of 95 per cent. alcohol are evaporated to dryness in the water-bath. The residue is repeatedly extracted with absolute alcohol, the alcoholic extract filtered into a flask, and the alcohol distilled off. The residue is then treated with about 70 c.c. of a saturated ethereal solution of oxalic acid, the precipitate of urea oxalate collected on a filter, washed with ether until free from oxalic acid, then dried at 70—80°, dissolved in water, and brought into the reaction vessel of the azotometer, where it is treated with alkaline hypobromite in the usual way.

Pflüger's Method.—Ten c.c. of the filtered urine are mixed with 30 c.c. of water and a sufficient quantity of a hydrochloric acid solution of phosphotungstic acid (100 c.c. of hydrochloric acid of sp. gr. 1.124 + 900 c.c. of phosphotungstic acid, 1 : 10). The mixture is warmed on the water-bath for 15 minutes, left in the cold for 4 hours (which is found to be long enough), made up to 100 c.c., and filtered through dry paper; 25 c.c. are placed in the azotometer, and made alkaline before introducing the tube containing the hypobromite. With these proportions, each c.c. of nitrogen (at 760 mm. and 15.5°) indicates 1 gram of urea per litre of urine. The author furnishes a table of corrections for other pressures and temperatures. M. J. S.

Estimation of Tannin. By LEOPOLD SPECHT and FRITZ LORENZ (*Chem. Zeit.*, 1900, 24, 170—171).—The method is based on the principle that saffranine is precipitated as a tannin-antimony lake, and

that the excess of saffranine may be readily titrated with solution of ammonium hyposulphite. The difference in c.c. between this estimation and the check experiment is the measure for calculating the amount of tannin.

The authors used as standard tannin a preparation from Schering and Co., "Acid tannic leviss," the moisture which it contained being allowed for. The ammonium hyposulphite was always prepared fresh by mixing 50 grams of zinc dust with 100 grams of water, and gradually adding 600 c.c. of ammonium hydrogen sulphite of sp. gr. 1.16, previously neutralised with ammonia; the temperature should not rise above 36°. After settling, 75 c.c. of the clear liquid are diluted to 2 litres, introduced into a reservoir, and covered with mineral oil. This reservoir is connected in the usual way with a burette, the end of which dips into the liquid to be titrated, which is also covered with mineral oil to exclude air.

L. DE K.

Soil Humus. Some Sources of Error in Analytical Methods. By A. L. EMERY (*J. Amer. Chem. Soc.*, 1900, 22, 285—291).—Hilgard's process for estimating humus in soils, which is frequently employed, briefly consists in extracting the soil, previously freed from calcium salts, with dilute ammonia. The solution is evaporated and the residue dried to constant weight in a platinum dish, the contents are then ignited and the dish weighed. The author has found that this process is not trustworthy, as the soil contains soluble organic matter which gradually combines with the ammonia, thus increasing the weight.

The use of a 4 per cent solution of potassium hydroxide has also been tried for the purpose of extracting the humus after first extracting the calcium salts with dilute hydrochloric acid. It was found, however, that aqueous potassium hydroxide liberates ammonia from the soil and that part of this enters into combination with the organic matter whilst another small portion escapes, so that the estimation of nitrogen contained in the humus gives results below the truth. The last source of error may be prevented by leaching the soil with 4 per cent. solution of aqueous potassium hydroxide in a funnel which is closed at the top with a stopper through which the leaching solution is admitted by a separating funnel. The glass support of a Gooch crucible serves very well for the funnel holding the soil. The solution from the soil is run directly into dilute sulphuric acid, the bottle containing this being sealed with a U-tube containing sulphuric acid. Gentle suction may be applied to hasten the process. It is also stated that humus is not quite insoluble in even very weak hydrochloric acid.

L. DE K.

Detection of Albumin in Urine. By ADOLF JOLLES (*Zeit. anal. Chem.*, 1900, 39, 146—147).—With certain urines poor in chlorides, the author's mercuric succinate test for albumin (*Abstr.*, 1896, 344) has proved to be deficient in sensitiveness unless sodium chloride is also added. It is therefore recommended that the amount of sodium chloride in the reagent should be doubled. In making the comparative test, water is added to the acidified urine instead of the reagent. The presence of mucin or nuclealbumin does not interfere with this test.

M. J. S.

General and Physical Chemistry.

Effects of Dilution, Temperature, and other Circumstances on the Absorption Spectra of Solutions of Didymium and Erbium Salts. By GEORGE D. LIVEING (*Trans. Camb. Phil. Soc.*, 1900, 18, 298—315).—Except for a slight difference in the absorption at the more refrangible end, the spectra of the different salts of the same metal in dilute solution are similar. For the chloride and sulphate, the spectrum is the same in different dilutions, so long as the thickness of absorbent is proportional to the dilution: the spectrum of nitrate solutions is modified slightly with increasing concentration. The first of these facts is in accord with Ostwald's view that the spectrum common to all the salts is due to the metallic ions, but the second is against this interpretation: so also is the fact that the intensity of the didymium and erbium bands is not affected by rise of temperature or by addition of the acid with the same negative ion. The author regards the metallic bands as the outcome of chemical actions between the molecules of the salt and of the solvent, whilst the general absorption at the more refrangible end may be due to encounters of molecules without chemical change. A certain interval of freedom is postulated between the rupture of a molecule and the recombination of its parts with each other or with parts of other molecules; during this interval, the parts have a capability of vibrating such as they do not possess in combination. Increased concentration and higher temperature will mean more frequent ruptures, more frequent recombinations, and shortening of the interval of freedom. These effects will compensate each other, and leave the average number of absorbent parts independent of the concentration and the temperature.

When alcohol or glycerol is the solvent, the bands are more diffuse and generally shifted towards the red. When dry hydrogen chloride is passed into the alcoholic solution, the colour changes from pink to bluish-green. The paper is illustrated by reproductions of the photographs obtained.
J. C. P.

Phosphorescence of Phosphoric Oxide. By HERMANN EBERT and BERTHOLD HOFFMANN (*Zeit. physikal. Chem.*, 1900, 34, 80—86).—Phosphoric oxide is capable of phosphorescence in a high degree, and it retains this property even when all impurities, such as the lower oxides, are carefully excluded. The commercial preparation after illumination shows, in addition to the greenish phosphorescence characteristic of the pentoxide, a pale glow, due probably to oxidation of the lower oxides present. The spectrum of the light emitted by the pure pentoxide is continuous, with a maximum intensity in the green, and the phosphorescence is much more intense at lower temperatures.
J. C. P.

Relation between the Constitution and Fluorescence of some Substances. By JOHN THEODORE HEWITT (*Zeit. physikal. Chem.*, 1900, 34, 1—19).—A fluorescent substance absorbs light of one wave-length, and emits light of another wave-length, so that two distinct sets of vibrations are involved. The author points out that for a compound which can exist in two tautomeric forms, and thus oscillates between two positions, the condition of fluorescence will most probably be satisfied. The most favourable cases would be those where there is a doubly symmetrical tautomerism, and consideration of a number of these shows that such compounds exhibit strong fluorescence. The various classes of fluorescent substances are considered in the order adopted by Meyer in his paper on the same subject (*Abstr.*, 1898, ii, 105). There are substances which, whilst possessing the requisite constitution, show no fluorescence; in such cases, it is possible (1) that the light emitted is beyond the visible part of the spectrum, or (2) that there is a secondary tautomerism which hides the primary. On the other hand, there are fluorescent substances which do not possess a doubly symmetrical tautomeric structure; in such cases, there may be a high velocity of transition from the one form to the other.
J. C. P.

Uranium Radiation. By HENRI BECQUEREL (*Compt. rend.*, 1900, 130, 1583—1585).—Part of the photographically active radiation from uranium is deflected in a magnetic field in the same direction as cathode rays.

When a small quantity of a barium salt is added to a uranium solution and then precipitated in the form of sulphate, the precipitate shows marked radioactivity, and hence it would follow that uranium commonly contains small quantities of a highly radioactive substance, probably actinium. At the same time, the most carefully purified uranium and its compounds still show radioactivity, and the extreme products of a long series of fractionations of uranium nitrate by Lecoq de Boisbaudran show identical radioactivity, whether it is measured by photographic effect or by its influence in promoting electrical discharge.
C. H. B.

Uranium Radiation. By HENRI BECQUEREL (*Compt. rend.*, 1900, 131, 137—138. Compare preceding abstract).—When solutions of uranium salts were treated with barium chloride and the barium subsequently precipitated as sulphate, the precipitate carried down a radioactive substance emitting rays which are deviated in the magnetic field. On repeating the precipitation, further quantities of this product were removed from the uranium solution, the amount decreasing with each successive operation. The uranium salt, when thus treated, was found to be less active, but the diminution in its activity decreased as the precipitations were repeated until, after the twelfth operation, its emissive power became approximately constant. The precipitations were still continued, but the variations were now found to be irregular, the uranium obtained after eighteen operations being decidedly less active than that from the twelfth. The rays emitted from the crude salt penetrate aluminium more readily than glass, whereas the converse holds with the radiations derived from the

purified compound. The electrical conductivity of air, as induced by the rays from uranium, is diminished by one-half after twelve precipitations, and its value is only one-sixth of the original after the eighteenth operation. G. T. M.

Photochemical Effects produced by the Hertzian Radiating Wire. By THOMAS TOMMASINA (*Compt. rend.*, 1900, 130, 1462—1465).—Luminous effects were observed about the radiating wire and these were photographed by placing the wire in direct contact with the sensitised gelatin plate. Illustrations are given showing the peculiar nature of the luminous radiations, and of the effect on them of iron and other metals, as well as of the differences resulting when the wire is sufficiently tense to also produce sound vibrations. L. M. J.

Modification of Metallic Surfaces under the Influence of Light. By H. BUISSON (*Compt. rend.*, 1900, 130, 1298—1300).—It is well known that metals exposed to ultra-violet radiations rapidly lose negative charges of electricity, being in this respect far more active when freshly cleaned. Light, however, causes a decrease of this activity, which is regained when the metal is kept for some time in the dark; this effect is very marked for amalgamated zinc. There is also a difference of potential between the surfaces of a darkened and illuminated metal, which may reach 0.125 volt. Most metals are more electro-negative after illumination, but the reverse obtains for platinum, whilst gold, silver, and iron are not affected. Red or yellow glass cuts off the rays effecting this change, but colourless glass does not, whilst ultra-violet rays have a reverse effect, so that the electric arc has little effect if not screened by colourless glass. The wavelength of the rays which separate the radiations thus acting in opposite directions is, for zinc, about 0.310μ . The action is not affected by the external atmosphere, similar results being obtained in hydrogen, carbon dioxide, &c. Amalgamated zinc, exposed to light through a screen and then exposed to iodine vapours, was also found to be least attacked in the illuminated portions, and hence to give an image of the screen.

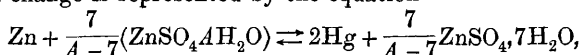
L. M. J.

Brazilin and Hæmatoxylin as Photographic Developers. By ROBERTO LEPETIT (*Bull. Soc. Chim.*, 1900, [iii], 23, 627—631).—Hæmatoxylin and brazilin, dissolved in aqueous sodium hydroxide, rapidly absorb atmospheric oxygen; the relative rapidity of absorption in the case of pyrogallol, quinol, hæmatoxylin, brazilin, and catechol is, with equal concentrations, given by the numbers 5:15:25:30:40. The rapidity with which the substances develop a photographic plate under similar conditions is determined by a similar ratio; pyrogallol, however, although more rapid than quinol, leaves the plate under developed to a greater extent than the latter. Catechol is wholly unsuitable for use as a developer. W. A. D.

Refutation of [Poynting's Theorem]. By P. S. WEDELL-WEDELLSBORG (*Zeit. physikal. Chem.*, 1900, 33, 631—635. Compare *Abstr.*, 1898, ii, 61).—A continuation of the author's previous papers on this subject, in which he holds that Poynting's theorem is erroneous on the following grounds. It is not in accord with the fundamental

laws of energy, with experimental results, with the laws of induction, and with modern theories of electrolysis. L. M. J.

Thermodynamics of Normal Cells. I. By ERNST COHEN (*Zeit. physikal. Chem.*, 1900, 34, 62—68).—On the basis of the equation $E = E_c/ne_0 + T.dE/dT$, and from the electrical measurements of Kahle, Jaeger and Wachsmuth, and of Callendar and Barnes, the author shows that the usual way of representing the process that goes on in the Clark cell is inadequate. Instead of $\text{Zn} + \text{Hg}_2\text{SO}_4 \rightleftharpoons 2\text{Hg} + \text{ZnSO}_4$, the essential change is represented by the equation



where A is the number of water molecules present for every one of ZnSO_4 in the saturated solution. If this is regarded as the true mechanism of the reaction, then thermochemical data give $E_c = 81127$ cal., whilst the electrical measurements give $E_c = 81490$ cal. Similarly, in the case where the zinc sulphate is present as hexahydrate, E_c from thermochemical sources is shown to be 75159 cal., whilst the electrical measurements lead to the value 75677 cal. J. C. P.

The Weston Cell as a Transition Cell and as a Standard of Electromotive Force, with a Determination of the Ratio to the Clark Cell. By H. T. BARNES (*J. Physical Chem.*, 1900, 4, 339—348).—The E.M.F.'s. of a number of Weston cells were determined at temperatures varying from 0 to 40°. Above 15°, the values of the temperature were in good accord with the formula $E_t - E_{15} = -0.086(t - 15^\circ)$, the values being in millivolts. Below 15°, the values were not concordant; the curves representing the E.M.F. as a function of temperature, however, all converged to 15° and agreed above this temperature. Experiments to see if a sudden change in the E.M.F. may occur below 15° led to varying results; in some cells, a rapid increase occurred in the neighbourhood of 2°, in others the rise of the E.M.F. was continuous. The ratio of the E.M.F. of the Weston cell at 20° to that of the Clark cell at 15° was found to be 1.40658, agreeing very closely with the ratio 1.40663 found by Dr. Kahle for the standard cells in the possession of the Reichsanstalt. L. M. J.

New Electrolytic Cell for Rectifying Alternating Currents. By W. L. HILDBURGH (*J. Amer. Chem. Soc.*, 1900, 22, 300—304).—The cell $\text{Cu} | \text{H}_2\text{SO}_4 | \text{Pt}$ allows currents of low voltage to pass if the copper is employed as the anode, but if the current is reversed owing to the high polarisation, no current passes if the voltage is not too great, and hence such a cell may be used as a rectifier for low voltage alternating currents. This is not a very efficient arrangement, however, and a better form consists of a plate of platinised platinum (A), partly in sulphuric acid, partly in hydrogen, and a platinum wire (P) sealed into glass under the acid; the whole is contained in a sealed vessel. Currents may pass from A to P, generating hydrogen at P, which escapes in bubbles joining the gas above the acid; in the opposite direction, however, polarisation occurs, P becoming coated with a film of oxygen. For high E.M.F.'s, a number of these cells in series may be employed. L. M. J.

Reversible Electrodes of the Second Order with Mixed Depolarisers. By A. THIEL (*Zeit. anorg. Chem.*, 1900, 24, 1—64).—The electrodes dealt with are of silver, and the depolarisers used are (1) mixed silver chloride and bromide, (2) mixed silver bromide and iodide. The equilibrium between silver chloride and bromide when precipitated together from mixed solutions of potassium chloride and bromide by a quantity of silver nitrate insufficient for complete precipitation has been studied by Küster (Abstr., 1899, ii, 205); the author has now made a similar investigation with mixed bromide and iodide. He concludes that silver chloride and bromide mix in all proportions, whilst silver bromide and iodide are miscible only within certain limits. In agreement with this, an electrode of the second order, with mixed silver chloride and bromide as depolariser, shows a 'mixed potential,' that is, a potential between the values obtained when the depolariser is pure chloride or bromide; the absolute value of the potential depends on the relative proportions of chloride and bromide. When the depolariser, on the other hand, is mixed bromide and iodide, the electrode shows the potential corresponding with the more soluble depolariser, so long as it is present. The values obtained for the solubility of the silver halogen salts agree well with those of Goodwin (Abstr., 1894, ii, 305). J. C. P.

Determination of Electrical Conductivity with Direct Current Instruments. By J. LIVINGSTON R. MORGAN and W. L. HILDBURGH (*J. Amer. Chem. Soc.*, 1900, 22, 304—307).—By the use of the rectifier described by Hildburgh (this vol., ii, 520), the resistance of electrolytes may be found, using a galvanometer or ammeter in place of the telephone. The method described by the authors is a substitution method; an alternating current passes through the liquid of which the resistance has to be determined, then through a set of resistance coils the terminals of which are also connected through the rectifier and a galvanometer. The reading of this instrument is noted, and the electrolyte replaced by a variable resistance which is adjusted until the same reading is observed. A more sensitive arrangement may be obtained by a differential wound galvanometer, one set of coils being in circuit with one rectifier, and the second similar opposed coils in circuit with a rectifier in the opposite direction. L. M. J.

Electrolytic Deposition of Metals from Non-aqueous Solutions. By LOUIS KAHLBERG (*J. Physical Chem.*, 1900, 4, 349—354).—In order to test whether Faraday's law is valid for non-aqueous solvents, solutions of silver nitrate in pyridine, aniline, phenyl cyanide, and quinoline were electrolysed, and the weight of silver deposited compared with that deposited from an aqueous solution in the same circuit; the weights respectively were as follows, those from the aqueous solutions being given first: 0.7836 gram, 0.7819 gram; 0.1788 gram, 0.1780 gram; 0.1612 gram, 0.1603 gram; 0.2501 gram, 0.2452 gram. In the quinoline solution, there was evidence of a complicated reaction, as the silver was carbonaceous; in the other solvents, it was firm and white. Experiments with lead and antimony gave very similar results. The work must be con-

sidered as preliminary, but it certainly tends to show that Faraday's law is valid for the non-aqueous solutions. It was found also that silver can be completely deposited in a compact white form from solutions in pyridine, or in aqueous pyridine by a current of density of from 0.17 to 0.25 ampere per 100 sq. cm. cathode area.

L. M. J.

Electrolysis of the Alkali Salts of Organic Acids. By JULIUS PETERSEN (*Zeit. physikal. Chem.*, 1900, 33, 99—120, 295—325, 698—720).—Compare Abstr., 1898, i, 352.

J. C. P.

Electrolysis through Semipermeable Membranes. By B. MORITZ (*Zeit. physikal. Chem.*, 1900, 33, 513—528).—The system, cathode | CuSO_4 solution | membrane 1 | K_4FeCy_6 solution | membrane 2 | CuSO_4 solution | anode, was electrolysed, and the polarisation was determined at membrane 2, where the semipermeable ferrocyanide was formed. The polarisation for primary currents of less than 0.3 milliampere was found to steadily increase and reach a maximum of 0.22 volt; with stronger currents, however, much higher values are attained. A formula is given for the polarisation as a function of time and its final maximum value, and is seen to satisfactorily reproduce the experimental values. A maximum of 1.006 volt was obtained for a primary current of 7.95 milliamperes per square centimetre, and the relative rates of change of polarisation and primary currents were found for various currents. Changes in the concentration of the solutions have but little effect on the polarisation, both in the above system and in that in which zinc sulphate replaces the copper sulphate. At first the copper ferrocyanide forms as a colourless film, this being most probably a supersaturated solution, and with weak currents this may remain for some hours, then becoming coloured brown with precipitation of the ordinary salt, whilst later, if the primary current exceeds about 0.2 milliampere per sq. cm., copper is precipitated. In the case of the zinc salt, however, this precipitation of the metal was not found to occur.

L. M. J.

Conductivity of Aqueous Solutions of Hydrochloric and Sulphuric Acids. By JAMES BARNES (*Trans. Nova Scot. Inst. Sci.*, 1900, 10, 129—138).—The author has calculated, by the method described by MacGregor (this vol., ii, 332), the conductivity of mixed solutions of hydrochloric and sulphuric acids, the assumption being made that the latter in moderately dilute solutions, as it does in very dilute solutions, dissociates into H and SO_4 ions. In the case of the solutions of from N to $2N$ concentrations, the calculated values are greater than those directly determined, whilst the reverse obtains for dilute solutions, but the differences in the latter case being almost within the experimental errors, the author considers that to seminormal concentrations the conductivity can be accurately calculated by MacGregor's method.

L. M. J.

Degree of Dissociation and Dissociation Equilibrium of Highly Dissociated Electrolytes. By HANS JAHN (*Zeit. physikal. Chem.*, 1900, 33, 545—576).—The determination of the degree of

dissociation by conductivity experiments involves the assumption that the ion velocities are independent of concentration: an assumption which has not been experimentally justified. The ion concentrations may, however, be compared by E.M.F. determinations, and in this case variations of velocity produce no effect. The author therefore determined the ion concentrations in solutions of potassium chloride, and by use of Kohlrausch's values for the conductivity obtained the ratios of the ion velocities at different concentrations. The velocity was found to decrease on dilution, so that ion concentrations calculated by the dilution law are necessarily too high, and values for E.M.F.'s calculated from the conductivity are considerably higher than the experimental values. The velocity had not reached its minimum at the concentration $N/300$, so that the ratio μ/μ_{∞} as a measure of dissociation is only valid for exceedingly dilute solutions. The values for the dissociation constant, as calculated from the conductivity values, also on this account decrease with dilution, but assuming complete dissociation at $N/600$, the values found from the E.M.F. determinations give a fairly constant value for the dissociation constant, the numbers varying irregularly from 0.14 to 0.10. Similar experiments were made and similar results obtained for solutions of sodium chloride and hydrogen chloride, and these elucidate the cause of the divergences from Ostwald's dilution law in the case of strong electrolytes.

L. M. J.

Electrochemical Equivalent of Carbon. By SIDNEY SKINNER (*Proc. Camb. Phil. Soc.*, 1900, 10, 261—267).—When a solution of potassium permanganate is electrolysed with a carbon anode, 77—86 per cent. of the gas liberated at the anode consists of carbon dioxide, the rest being carbon monoxide and oxygen. The total volume of gas liberated is nearly the same as the volume of oxygen liberated by the same current in a dilute sulphuric acid voltameter; the permanganate ion persists in solution even although a quantity of electricity more than sufficient for its complete decomposition is passed through the cell. The author finds the electrochemical equivalent of carbon to be three times that of hydrogen.

A cell may be constructed with a carbon rod in potassium permanganate, and a lead peroxide plate in dilute sulphuric acid, the two electrolytes being separated by a porous pot: the E.M.F. is 0.33 volt, and acts externally from the lead peroxide to the carbon. In this self-acting system, carbon is consumed at the ordinary temperature.

J. C. P.

Thermo-electrical Properties of Alloys. By ÉMILE STEINMANN (*Compt. rend.*, 1900, 130, 1300—1303).—The thermo-electromotive forces of junctions of pure lead with various alloys were determined, the alloys employed being ten varieties of nickel-steel, four of platinum-iridium, three of aluminium-bronze, five of bronze, five of brass, and four of German silver. The determinations were made with the hot junction at 55°, 95°, 140°, 195°, and 260°, the cold junction being in all cases at 0°. Tables of the values contained are given, and it is seen that the curves of the E.M.F. of the alloys would always lie either entirely within or entirely without those of the pure components, but the

position of the curve cannot be calculated from the percentage composition. No simple rule appears to connect the E.M.F. with the composition, and very small quantities of one metal may change very considerably the E.M.F. of another, this being very marked in the case of the addition of nickel to iron.

L. M. J.

Thermo-electricity of Certain Alloys. By ÉMILE STEINMANN (*Compt. rend.*, 1900, 131, 34).—Nickel steel containing 36.1 per cent. of nickel has between 0° and 100° an E.M.F. of -2461 microvolts; the E.M.F. developed from a specimen containing 28 per cent. of this metal between 20° and 260° is 385—386 microvolts, lead being in both cases the standard of comparison.

G. T. M.

Transparency of various Liquids to Electric Oscillations. By A. DE HEEN (*Compt. rend.*, 1900, 130, 1460—1461).—The liquids examined may be thus divided with regard to their transparency to electric oscillations: opaque—water, ethyl alcohol, amyl alcohol, aldehyde, carbon disulphide, ethyl bromide; transparent—ether, petroleum, benzene, xylene, butyric acid, valeric acid. For pure liquids there appeared to be no gradation, the liquid being either almost completely opaque or completely transparent, but with mixtures gradation may be obtained; 8 per cent. of alcohol reduces the transparency of ether to one-half, and 30 per cent. renders it quite opaque.

L. M. J.

Electromagnetic Rotation of the Plane of Polarisation in Solutions of Salts and Acids. By J. FORCHHEIMER (*Zeit. physikal. Chem.*, 1900, 34, 20—30).—Perkin has found that with falling concentration the molecular rotation of sulphuric acid solutions diminishes, whilst that of hydrochloric acid solutions increases. Oppenheimer (*Abstr.*, 1899, ii, 139) has shown that the molecular rotation of alkali bromides and chlorides is independent of the concentration of the solution. The author confirms Perkin's observations as to the acid solutions, and finds that the molecular rotation of ammonium, sodium, and magnesium sulphates is independent of the concentration, whilst that of lithium sulphate increases with falling concentration. Lithium chloride, as noticed by Perkin (*Trans.*, 1894, 65, 20), and confirmed by the author, behaves in a similar fashion. The molecular rotation of cadmium bromide and iodide does not vary with the concentration of the solutions, and is therefore independent of the electrolytic dissociation.

J. C. P.

Permanent Change and Thermodynamics. By PIERRE DUHEM (*Zeit. physikal. Chem.*, 1900, 33, 641—697).—A mathematical paper not suitable for abstraction.

J. C. P.

Specific Heats of Metals and the Relation of Specific Heat to Atomic Weight. By WILLIAM A. TILDEN (*Phil. Trans.*, 1900, A, 194, 233—255).—The specific heats of pure cobalt and pure nickel have been determined in Joly's steam calorimeter. The atomic weights and densities of these metals are close together, but the mean specific heat of cobalt between 15° and 100° is 0.10303, and that of nickel 0.10842. If 58.55 and 58.24 are taken as the atomic weights of

cobalt and nickel respectively, the corresponding atomic heats are 6.03 and 6.31. In the case also of gold and platinum, two metals whose atomic weights and densities are not very different, the atomic heats have quite different values, so that Dulong and Petit's law is not strictly applicable.

Determinations of the specific heat of various specimens of iron and copper show that the presence of a non-metallic impurity raises the specific heat of a metal; a non-metal as impurity has much more influence than a metal which produces little effect until the quantity is large enough to make itself felt through the difference in atomic weight.

A series of experiments have been made with cobalt and nickel at the temperatures of solid carbon dioxide (-78.4°), and boiling oxygen (-182.5°). The mean specific heats of the two metals for the various ranges of temperature are as follows:

Range.	Specific heat.	
	Cobalt.	Nickel.
100° to 15°	0.10303	0.10842
15° „ -78.4°	0.0939	0.0975
15° „ -182.5°	0.0822	0.0838
By calc. -78.4° „ -182.5°	0.0712	0.0719

It is seen that the specific heat of nickel falls more rapidly than that of cobalt, and that the two specific heats approach each other. For the range last given, the mean atomic heat of both metals would be 4. J. C. P.

Specific Heats of Fluids. By ÉMILE H. AMAGAT (*Compt. rend.*, 1900, 130, 1443—1447).—The pressure coefficient of the specific heat at constant volume is given by the expression $dc/dp = -AT.d^2v/dt^2$, and from the complete set of isothermals for carbon dioxide between 0° and 260° , and from 1 to 1000 atmos., the author has constructed the curves for d^2v/dt^2 for various temperatures and pressures from which the variations of the specific heat at constant volume can be deduced. The curves show that this constant increases with pressure, reaches a maximum, and then decreases, the pressure at which the maximum occurs increasing with temperature. Below the critical temperature, the curve consists of two separated portions, and the author gives a form of expression for the calculation of the difference between the specific heats in the liquid and gaseous states. L. M. J.

Thermal Conductivity of Nitrogen Peroxide as affected by Change of Temperature and Pressure. By GAETANO MAGNANINI and V. ZUNINO (*Gazzetta*, 1900, 30, i, 405—435. Compare Magnanini and Malagnini, *Abstr.*, 1898, ii, 282).—The former experiments (*loc. cit.*) on the thermal conductivity of air, hydrogen, carbon dioxide, and nitrogen peroxide are extended to pressures greater than that of the atmosphere. The results show that, as before, air, hydrogen, and carbon dioxide obey Newton's law, the expression $1/t \cdot \log.(d_1 - d_0/d - d_0)$ having a constant value. For nitrogen peroxide, which dissociates on heating, this is not the case, but the numbers obtained are in complete accord with the kinetic theory of gases. Thus, at high temperatures,

the conductivity of nitrogen peroxide is less than that of hydrogen, whilst for temperatures at which the change in the amount of dissociation is greatest, the conductivities of the two gases are about equal. T. H. P.

Effect of very Low Temperatures on the Colour of Compounds of Bromine and Iodine. By J. H. KASTLE (*Amer. Chem. J.*, 1900, 23, 500—505).—On cooling to the temperature of liquid air, a marked decrease occurs in the intensity of colour of lead iodide, phosphorus pentabromide and heptabromide, mercuric bromoiodide, iodoform, benzenedibromosulphonamide, tribromophenol bromide, mercuric iodide, bromine, iodine in solution in alcohol or carbon disulphide, sulphur, red-phosphorus, chrome alum, manganous chloride, chromic chloride, and alkaline alcoholic solutions of phenolphthalein and *p*-nitrophenol: the colour in many cases disappears altogether. No change was observed in the colour of solid iodine and of hydrated copper sulphate. T. M. L.

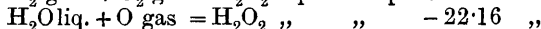
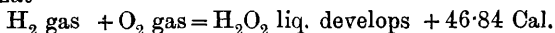
Minimum in the Molecular Lowering of the Freezing Point of Water, produced by Certain Acids and Salts. By VICTOR J. CHAMBERS and JOSEPH C. W. FRAZER (*Amer. Chem. J.*, 1900, 23, 512—520. Compare Jones and Chambers, this, vol., ii, 262).—Minima in the molecular lowering of the freezing point of water occur in the case of phosphoric acid at about 0.5*N*, hydrochloric acid and sodium acetate between 0.1*N* and 0.2*N*, zinc chloride and strontium iodide at about 0.1*N*, and a less defined minimum in the case of copper sulphate at about 0.9*N*. T. M. L.

Depression of the Freezing Point by Mixtures of Electrolytes. By JAMES BARNES (*Trans. Nova Scot. Inst. Sci.*, 1900, 10, 139—161).—In order to test Macgregor's formulæ (this vol., ii, 332), the author has compared the freezing point depressions in the case of mixtures of potassium, sodium, and hydrogen chlorides with those obtained by calculation by Macgregor's method. The details of the experiments are given, and it is seen that the author's results for the separate solutions agree well with those of Loomis. The values found for double and triple mixtures agree well with those calculated, and hence indicate the availability of the formulæ in question. L. M. J.

Heat of Neutralisation of Hydrogen Peroxide by Lime. By ROBERT DE FORCRAND (*Compt. rend.*, 1900, 130, 1250—1251. Compare this vol., ii, 277).—The heat production, due to the addition of a solution of lime to solutions of hydrogen peroxide of varying concentration, was determined. Curves for heat produced against concentration of hydrogen peroxide were found to consist of three straight lines meeting at points corresponding with $\text{CaO}, 2\text{H}_2\text{O}_2$ and $\text{CaO}, 10\text{H}_2\text{O}_2$. The former indicates the production of the peroxide $\text{CaO}_2, \text{H}_2\text{O}_2$, or $\text{Ca}(\text{O}\cdot\text{OH})_2$, and the heat of formation is calculated as 7.42 Cals. L. M. J.

Heat of Dissolution of Hydrogen Peroxide: Thermal Value of the Hydroxyl Function; Influence of Hydrogen and Carbon. By ROBERT DE FORCRAND (*Compt. rend.*, 1900, 130, 1620—1622).—Hydrogen peroxide solutions containing from 35.31 to

85.93 per cent. of the peroxide gave heats of dissolution ranging from +0.071 Cal. to +0.403 Cal., and the curve representing these results shows that there is a definite hydrate of the composition $\text{H}_2\text{O}_2 + \text{H}_2\text{O}$, whilst the heat of dissolution of the pure peroxide is +0.46 Cal. It follows that



The heat of fusion calculated from that of water is -2.70 Cal., and the same value is obtained by taking the mean heat of fusion of water and glycerol.

Combining these results with the known results of the action of hydrochloric acid on sodium hydroxide and peroxide and the action of sodium on water, it follows that

$\text{H}_2\text{O}_2 \text{ sol.} + \text{Na}_2 \text{ sol.} = \text{H}_2 \text{ gas} + \text{Na}_2\text{O}_2 \text{ sol. develops } +68.15 \text{ Cal.}$, and hence the mean thermal value of the hydroxyl function in the solid state is +34.07 Cal. Comparison with the corresponding values in the case of glycol leads to the conclusion that this value is affected by the proximity of various elements, or groups of elements, in the same molecule.

C. H. B.

Acidity of Alcohols. By ROBERT DE FORCRAND (*Compt. rend.*, 1900, 130, 1758—1761. Compare preceding abstract).—In a former communication, the author expresses the acidic functions of water, hydrogen peroxide, and glycol in terms of the heat developed when the hydroxylic hydrogen is replaced by metallic sodium, the values for H_2O , $\frac{1}{2}\text{H}_2\text{O}_2$, and $\frac{1}{2}\text{C}_2\text{H}_4(\text{OH})_2$ being +31.19, +34.07, and +31.32 Cal. respectively. By subtracting the second of these constants from the third, the number -2.75 is obtained; this quantity is characteristic of the group CH_2 , and is called its "coefficient of influence."

The coefficients of influence of carbon, hydrogen, methyl, and methenyl CH are deduced in a similar manner, their values being +3.01, -2.88, -5.63, and +0.13 Cal. respectively.

By applying this reasoning to the homologous series of alcohols, the coefficients +28.4, +25.69, and $(28 - 2.75 \times n)$ are obtained respectively for the first two members and the general term. It follows from this that the C_4 alcohol should not possess any acidity; this, however, is not the case, and the anomaly probably arises from the fact that the calculated coefficients of the two lowest members are less than the experimental values. Moreover, in straight chain compounds, the influence of a radicle probably diminishes as the distance from the hydroxyl group increases. The latter hypothesis is confirmed by a thermochemical study of the acidity of trimethylcarbinol and malonic and succinic acids. The calculated difference between the acidities of malonic and succinic acids is 1.375 Cal., whereas the actual difference is only 0.730 Cal., or 1.375×0.535 Cal. Similarly, the difference between the observed acidity of trimethylcarbinol and the calculated value for $\text{C}\cdot\text{OH}$ should be 3×5.63 Cal.; it is, however, only $3 \times 5.63 \times 0.585$ Cal. Taking 0.56 as the mean factor of correction, this quantity is employed in accordance with the following rule.

When an acidic group is situated in an open chain compound, the

influence of any other radicle of the compound on the acidity is only 0·56ⁿ of what it would be if this radicle were directly attached to the acidic group.

When this correction is applied to the alcohols, the calculated values of the coefficients of acidity approximate fairly closely to those obtained by direct experiment.

G. T. M.

General Theory of Acidity. By ROBERT DE FORCRAND (*Compt. rend.*, 1900, 131, 36—40. Compare preceding abstracts).—In extending the generalisations put forward in two previous communications, the author calculates the “coefficients of acidity” and “influence” for a series of organic and inorganic radicles. The calculated coefficients agree fairly closely with those determined experimentally, and although this theory of acidity is still incomplete, it should be possible, knowing the constitution of any compound containing acidic hydrogen, to deduce by the aid of the “coefficients of influence” either the acidity or the heat of fusion of the substance. The coefficients of acidity of carboxyl and hydroxylic hydrogen are +52·62 and +18·43 Cal. respectively; the coefficients of influence of carbonyl, hydroxylic oxygen, sodium, and sodoxyl, NaO, are +18·55, +15·54, -45·70, and -30·16 Cal. respectively. The calculated acidities of (solid) propionic, *n*-butyric, and *n*-valeric acids are +49·32, +49·23, and +49·20 Cal. respectively, whilst the experimental values for the first two in the liquid state are +52·46 and +52·36 Cal. The experimental and calculated values for malonic, succinic, and glyoxylic acids are practically identical. The coefficients of influence of sulphur, nitrogen, and phosphorus in their oxy-acids are +16·79, +2·25, and +30·39 Cal. respectively. The acidity of formic and oxalic acid is abnormally high, the calculated values of this constant being +51·01 and +52·62, whilst the experimental numbers are 53·69 and 57·70, respectively. This abnormal acidity may be due to association. The theory of acidity cannot, however, be applied to cyanogen derivatives and hydrazids.

G. T. M.

Temperature Coefficient of Ester Hydrolysis. By T. SLATER PRICE (*Öfvers. K. Vet. Akad. Stockholm*, 1899, 56, 921—934).—The rate of hydrolysis of a number of esters in presence of *N*/4 hydrochloric acid has been determined at various temperatures from 0° to 50°. The results obtained agree closely with those required for the formula $\log k = -A/T + B$, and are summarised in the following table:

Ester.	Value of <i>A</i> .	<i>k</i> at 40°.
Methyl acetate.....	8663	0·006397
Ethyl acetate	8695	0·006485
Propyl acetate	8586	0·006497
<i>iso</i> Butyl acetate	8746	0·006461
Methyl propionate	8273	0·006898
Propyl formate	7409	0·01554

The value of *A* for esters of the same acid is the same; for esters of the same alcohol, *A* varies (compare Hemptinne, Abstr., 1894, ii, 274; Löwenherz, Abstr., 1895, ii, 107).

J. C. P.

Vapour Pressure Relations in Mixtures of Two Liquids. I. and II. By A. ERNEST TAYLOR (*J. Physical Chem.*, 1900, 4, 290—305 and 355—369).—The boiling points and composition of the vapour were determined for mixtures of acetone and water at various pressures. The first paper contains only an account of the methods employed. The author shows that superheating is very difficult to avoid, and considers that sufficient precautions have not been taken in the past, especially as the superheating can frequently only be detected by varying the conditions of the experiment. A mixture of garnets with platinum or silver tetrahedra was found to be most effective for preventing superheating, but these, or any other substance used for the same purpose, must be present in large quantities, their volume being at least one-half that of the liquid.

The second paper contains solely the vapour pressure curves and the numerical data for mixtures of acetone and water, all theoretical considerations and the discussions being postponed to a later paper. Some points are, however, noticeable; for example, the great steepness of the acetone curve compared with that of water, so that the curves are much closer at low temperatures and spread out as the temperature rises. Further, the composition of the vapour at low concentrations is markedly different from that of the solution. Thus, when the solution contains about 10 per cent. of acetone, the vapour contains 80 per cent. These points, however, will probably be fully discussed in later papers.
L. M. J.

Absorption of Nitrogen and Hydrogen by Aqueous Solutions of Dissociating Substances. By LEONHARD BRAUN (*Zeit. physikal. Chem.*, 1900, 33, 721—739).—The author has determined the absorption coefficients of nitrogen and hydrogen at temperatures between 5° and 25° for aqueous solutions of the non-electrolytes, carbamide, and propionic acid, and the electrolytes, sodium and barium chlorides. The relation $C_1/C_2 = 1$, where C_1 is the molecular concentration of the gas in pure water, C_2 that in the solution of an indifferent substance, at the same temperature and partial pressure, is satisfied in the case of carbamide and propionic acid, but is quite inapplicable to sodium and barium chlorides. For the solutions of the latter compounds, the empirical relation $(\alpha - \alpha')/Gm^{2/3} = \text{const.}$ is found to hold; here α and α' are the absorption coefficients in water and solution respectively, whilst Gm is the number of gram-molecules per unit of volume.

Compare the results obtained by Steiner (Abstr., 1894, ii, 345), Gordon (Abstr., 1896, ii, 154), and Roth (Abstr., 1898, ii, 18).

J. C. P.

Temperature of Maximum Density of Solutions of Ammonium Chloride, Lithium Bromide, and Lithium Iodide. By LOUIS C. DE COPPET (*Compt. rend.*, 1900, 131, 178. Compare Abstr., 1899, ii, 590).—The results are exhibited in tabular form. G. T. M.

Isohydic Solutions. By WILDER D. BANCROFT (*J. Physical Chem.*, 1900, 4, 274—289).—It is commonly considered that by the mixing of isohydic solutions, no dissociation change occurs, and similar considerations have been applied to dissociation in gases, that

is, the dissociation is supposed to be unaltered by the addition of one of the products of dissociation at the same pressure as its partial pressure in the system, also termed "isohydric." These considerations have, however, only limited validity as considered from the point of view of the mass-action law; it is shown that by the addition of "isohydric" hydrogen to a dissociated system of hydrogen iodide, the dissociation is decreased, whilst the addition of isohydric carbon dioxide to ammonium carbamate causes an increase of dissociation. The general case is investigated, and it is deduced that if the dissociation is represented by $aA = bB + cC + \dots mM$, and isohydric B is added, the dissociation is unchanged, decreased, or increased according as a is equal to, greater, or less than $b + c + \dots m - b$. Similar considerations hold for electrolytic dissociation; if the dissociation be $A_1 = bB_1 + cC_1 + eM_1$, and $A_2 = fB_1 + gC_2 + \dots hM_2$, then the dissociation will be unchanged if $b + c + \dots e = 1$ and $f + g + \dots h - f = 1$, but if either of these expressions be greater than unity, the dissociation of the corresponding salt will be increased, and conversely. In the case of strong electrolytes, the mixture of isohydric solutions must generally be accompanied by dissociation changes. It is calculated that by the mixture of equal volumes of $N/100$ solutions of potassium and sodium chlorides, a decrease of dissociation should occur for each salt; conductivity experiments, however, showed an increase of dissociation. This is apparently not in accord with Arrhenius' results (this vol., ii, 201), but the discrepancy is explicable in view of the results obtained by Jones and Knight, which prove that dissociation is decreased by the mixture of strong solutions, but increased by the mixture of dilute solutions of potassium and ammonium chlorides (Abstr., 1899, ii, 628). The results are still not in accord with the theoretical deductions, and it is possible that the explanation has to be sought for in the effect of the undissociated products on dissociation.

L. M. J.

Solubility of Mixtures of Salts having one Common Ion. By CHARLES TOUREN (*Compt. rend.*, 1900, 130, 1252—1254).—The solubility curve of potassium chloride in solutions of potassium bromide is not identical with that for the solubility in solutions of potassium nitrate, so that the two latter salts have not equal effects on the solubility of the chloride. The solubility curve for potassium bromide in solutions of potassium chloride was also determined, and it was found that these curves do not cut, but form one continuous curve. There is hence no point at which the two salts are in equilibrium with the solution, and but one solid phase exists at all concentrations, that is, mixed crystals of the two compounds are formed. The author points out that solubility determinations may hence be of value in cases of doubtful isomorphism (this vol., ii, 396).

L. M. J.

Solubility of Hydrated Mixed Crystals. III. By WILLEM STORTENBEKER (*Zeit. physikal. Chem.*, 1900, 34, 108—123).—A study of the mixed salts, cadmium and ferrous sulphates, and copper and manganese sulphates, on the lines of the author's previous work (Abstr., 1896, ii, 13; 1897, ii, 250). The limits for cadmium and ferrous sulphates are found to be:

	(CdFe)SO ₄ , 2½H ₂ O.	(CdFe)SO ₄ , 7H ₂ O.
Solution...	100—79·8 mol. per cent. Cd.	79·8—0 mol. per cent. Cd
Crystals...	100—99·1 " "	36·6—0 " "

Similarly, for copper and manganese sulphates, the limits are :—

	(CuMn)SO ₄ , 5H ₂ O.	(CuMn)SO ₄ , 7H ₂ O.
Solution	100—15·9 and 10·27—0 mol. per cent. Cu.	15·9—10·27 mol. per cent. Cu.
Crystals	100—22·9 and 10·5 —0 " "	23·5—16·0 " "

In the last case, the solubility isotherms cut each other in two points.
J. C. P.

Separation in Alloys. By G. NANNES (*Öfvers. K. Vet. Akad. Stockholm*, 1899, 56, 735—744).—When a molten alloy of equal parts of lead and tin is kept in a bath so that the two ends of the containing tube are at different temperatures, the concentration of the tin increases at the cooler end. This phenomenon is observed in both vertical and horizontal tubes, although in the former the point of equilibrium is reached more rapidly, and the final difference in concentration is somewhat greater than in the latter. The melting point curve of lead-tin alloys shows that in a 50 per cent. alloy the lead is to be regarded as the solvent; the observations, therefore, agree with Soret's rule that, in a homogeneous solution, the parts of which are kept at different temperatures, the warmer part becomes more dilute and the cooler part more concentrated with regard to the solute. On the other hand, the final concentrations at the ends of the tube are not exactly in the inverse ratio of the absolute temperatures, as required by van't Hoff's theory.
J. C. P.

Formation of Oceanic Salt Deposits, particularly of the Stassfurt Beds. XVIII. Gypsum and Anhydrite. I. The Hydrate CaSO₄, ½H₂O. By JACOBUS H. VAN'T HOFF and E. F. ARMSTRONG (*Sitzungsber. K. Preuss. Akad. Wiss.*, 1900, 28, 559—576).—The hydrate CaSO₄, ½H₂O is conveniently prepared by warming 20 grams of gypsum with 50 c.c. of nitric acid of sp. gr. 1·4 for 18 hours at 40°; the crystals obtained are freed from acid by decantation, washed with alcohol, and dried.

The relative stability of the hydrates CaSO₄, 2H₂O and CaSO₄, ½H₂O can be deduced theoretically from their vapour tension curves, but previous researches have shown that the extreme slowness with which equilibrium is reached prevents an accurate and trustworthy determination of the vapour tension. The process may, however, be accelerated by the agency of solutions of sulphuric acid, nitric acid, sodium chloride, and magnesium chloride. The results obtained with solutions of sulphuric acid are not so satisfactory, probably owing to the comparative insolubility of calcium sulphate in the acid.

When sodium chloride is gradually added to water in the presence of gypsum, the boiling point rises regularly to the temperature at which the gypsum is converted into the hydrate CaSO₄, ½H₂O. Further addition of sodium chloride at this point produces no further rise of temperature until the conversion is complete. A similar constant level in the boiling point curve is obtained when a concentrated solution of sodium chloride and the hydrate CaSO₄, ½H₂O is diluted.

In this way, the conversion temperature is determined to be 101.45° , at which point the vapour tension of the hydrate $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ is equal to an atmosphere. At 77.1° , by a similar experiment under reduced pressure, the tension is found to be 238 mm. At 25° , by moistening with magnesium chloride solutions of various concentrations, the tension is found to be 9.1 mm. From two of these values, and with the help of the equation $\log_e(p_g/p_w) = -q/2T + \text{const.}$, the vapour tension of the hydrate $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ is calculated for intermediate temperatures; in this equation, p_g and p_w are the vapour tensions of the hydrate $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ and water respectively; q is the heat liberated when 18 kilograms of water unite with the hydrate $\text{CaSO}_4 \cdot \frac{1}{2}\text{H}_2\text{O}$ to form gypsum.

It is a consequence of the above equation that at 107° $p_g = p_w$, and this point has been experimentally determined by the help of a dilatometer. Gypsum is therefore a compound whose melting point (107°) lies above its boiling point (101.45°). The conversion of $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ into $\text{CaSO}_4 \cdot \frac{1}{2}\text{H}_2\text{O}$ accounts for the apparent diminished solubility of gypsum above 100° .

J. C. P.

Equilibria in the Partition of an Acid between Ammonia and Sparingly Soluble Metallic Hydroxides. By W. HERZ (*Zeit. anorg. Chem.*, 1900, 24, 123—126).—Beryllium hydroxide is apparently insoluble in ammonium salts, and therefore unsuited for investigation on the lines of the author's previous work (*Abstr.*, 1899, ii, 752; 1900, ii, 68 and 337).

The equilibrium represented by the equation $\text{Cd}(\text{OH})_2 + 2\text{NH}_4\text{NO}_3 \rightleftharpoons \text{Cd}(\text{NO}_3)_2 + 2\text{NH}_4\text{OH}$, has been studied, and the results are similar to those obtained in the case of zinc (*loc. cit.*). An empirical expression of the type formerly employed fits in better with the experimental results than the expression deduced from the law of mass action.

J. C. P.

Molecular Transformation of Cinchonine; An Addition to the Theory of Catalytic Action. By RUDOLF WEGSCHEIDER (*Monatsh.*, 1900, 21, 361—387).—It is shown that the transformation of cinchonine by means of halogen acids into α -isocinchonine (Skrap, *Abstr.*, 1899, i, 961) is an example of the case of auxiliary reactions considered by the author (this vol., ii, 199), but the mathematical discussion does not lend itself to abstraction. The author puts forward the view that catalytic acceleration of a chemical reaction in a homogeneous solution can be explained by assuming that there is a continuous succession of intermediate stages, which the catalytic agent is able to influence by reversible reactions with the substances present, and so bring about or accelerate the main reaction.

R. H. P.

Theory of Catalytic Reactions. By HANS EULER (*Öfvers. K. Vet. Akad. Stockholm*, 1899, 56, 309—333).—A general discussion of reaction velocity and the part played by catalytic agents. It is pointed out that there are no grounds for making a distinction between electrolytes and non-electrolytes, and the author regards all chemical substances as electrolytes. The study of the influence of the solvent and the temperature makes it probable that substances hitherto

regarded as non-electrolytes react through intermediary ions. Every catalysis is supposed to consist in an increase in the number of the ions concerned in the accelerated reaction. The author applies his theories to the special case of ester formation and decomposition.

J. C. P.

The Driving Tendency of Physicochemical Reaction and its Temperature Coefficient. By THEODORE W. RICHARDS (*J. Physical Chem.*, 1900, 4, 383—393).—The paper contains essentially a slightly modified treatment of the van't Hoff equation. It is pointed out that the study of pressure affords a more direct method of analysing the progress of a reaction than that of volume or concentration. The author uses the term 'reaction-metatherm' to indicate the relation between pressure and temperature in the equilibrium ratio. In the expression, which is of the form $d/dT \log. p_1^{n_1} \dots T^n / p_2^{n_2} \dots = U/RT^2$, U represents the actual heat evolved, and is hence an expression of the theorem of Le Chatelier. The expression $\log. p_1^{n_1} \dots / p_2^{n_2} \dots = k$ is that which represents the reacting tendency of the reaction at a certain temperature, and receives the name of the "driving tendency" of the reaction.

L. M. J.

G. Linck's Crystallographic Views. By WILHELM MUTHMANN (*Ber.*, 1900, 33, 1771—1774).—A criticism of Linck's proposal to correct the atomic weights of elements by the aid of crystallographic considerations (compare Abstr., 1899, ii, 415).

W. A. D.

Additive Nature of the Properties of Atoms. By STEFAN MEYER (*Ber.*, 1900, 33, 1918—1919).—According to the author, only those compounds whose molecular volumes are the true sum of the atomic volumes of their constituent elements possess properties which are the actual sum of the atomic properties of their constituents. When, in the formation of the compound, volume contraction or dilatation occurs, other physical constants, for example, magnetisation number (Abstr., 1899, ii, 587; 1900, ii, 7, 143, 385), molecular heat (Abstr., 1900, ii, 464), &c., vary from the true sum in the direction of the maximum or minimum of the atomic volume curve.

J. J. S.

Second Report of the Committee of the German Chemical Society on Atomic Weights. By the Members of the Committee: HANS LANDOLT, WILHELM OSTWALD, and KARL SEUBERT (*Ber.*, 1900, 33, 1847—1883. Compare Abstr., 1899, ii, 86).—This report deals with the conclusions arrived at by the International Commission formed to consider atomic weights (*Ber.*, 1898, 31, 2949). The members of the Commission agree almost unanimously that the atomic weight of oxygen shall be taken as the standard, and equal to 16.00; the advantages of this value are dealt with in detail in the report. The atomic weights are to be given with so many decimals that the last figure is *certainly* correct to less than half a unit; calculations made with these weights will thus be of permanent value, and subject to no alteration as additional accuracy is obtained in future determinations.

W. A. D.

True Atomic Weights of Ten Elements Deduced from Recent Researches. By GUSTAVUS HINRICHS (*Compt. rend.*, 1900, 131, 34—36. Compare preceding abstract).—The author states that by employing his method of calculation (*Abstr.*, 1893, ii, 317), the exact atomic weights of hydrogen, carbon, oxygen, sulphur, chlorine, bromine, sodium, silver, barium, and boron are found to be very close to the values in ordinary use. The values of these constants published by the German Committee on atomic weights are incorrect, and by employing these data Gautier has introduced an error into his determination of the atomic weight of boron
G. T. M.

Thiele's Theory of Partial Valencies in the Light of Stereochemistry. By EMIL KNOEVENAGEL (*Annalen*, 1900, 311, 194—240).—An attempt to place a stereochemical interpretation on Thiele's theory of partial valencies (*Abstr.*, 1899, i, 554). The author's speculations involve the hypothesis that the difference between a double and a single linking depends on the intramolecular movements of the atoms concerned.
M. O. F.

The Steric Aspect of Partial Valencies. By JOHANNES THIELE (*Annalen*, 1900, 311, 241—255).—A criticism of the foregoing paper, in which the author regards the Wunderlich model, employed by Knoevenagel in his discussion, as unsuitable for the further development of valency relations.
M. O. F.

Lecture Experiments. Reversible Chemical Reactions. By W. LASH MILLER, and FRANK B. KENRICK (*J. Amer. Chem. Soc.*, 1900, 22, 291—300).—A number of incomplete reactions capable of being employed for lecture experiments illustrative of reversible reactions are described. An orange solution of ferric chloride with ammonium thiocyanate in equivalent quantities becomes dark red by the addition of excess of either compound, and colourless by addition of ammonium chloride, whilst the same solution also may be used to illustrate the effect of dilution. The reactions between bismuth chloride and water, and of ammonium with salts of copper or silver, are also suitable for lecture purposes. The dissociation of water vapour may be shown by heating platinum wire by means of an electric current in the neck of an ordinary distilling flask, and ammonia may be similarly dissociated. The change from sodium sulphate to sodium chloride and *vice versa* by the addition of the respective acids may be conveniently shown on the screen, the crystallisation taking place on lantern slides. The reaction between antimony chloride and hydrogen sulphide is also suitable for lecture purposes, and in this case the effect of temperature and pressure is also well seen. The authors describe a form of pressure pump for use in connection with the water mains by means of which a gas can be brought to the pressure of the mains in three or four strokes of the pump without coming into contact with any liquid.
L. M. J.

Method for Testing Weights. By THEODORE W. RICHARDS (*Zeit. physikal. Chem.*, 1900, 33, 605—610).—An account of the method in use in the author's laboratory for testing and correcting for the relative value of weights employed in quantitative work. The

author does not claim any originality for the method, but insists strongly on its necessity in all quantitative determinations.

L. M. J.

Receiver for Fractional Distillation in a Vacuum. By LUCIEN FOGETTI (*J. Amer. Chem. Soc.*, 1900, 22, 360—361).—The new receiver consists of three separator funnels sealed together, each of the three bulbs being furnished with a side stopcock, the uppermost having an additional one which is connected with the vacuum pump. The condenser tube enters into the top bulb, connection being made by a ground glass joint or a rubber stopper if desired. The two stopcocks of the bottom funnel are closed, also the side stopcock of the middle funnel and the left side stopcock of the top funnel. The other stopcocks are opened and the second side stopcock of the top funnel is connected with the vacuum pump. When the first fraction has collected in the lower funnel, the stopcock of the middle funnel is closed and the second fraction collected; the stopcock of the middle one is then closed and the third fraction collected in the top funnel.

The bottom funnel is emptied by opening both stopcocks. The lower one being again closed, the side one is connected with a second pump and the vacuum is restored. By opening the stopcock of the middle funnel, its contents flow into the bottom one and the operation is then repeated.

L. DE K.

Inorganic Chemistry.

Hydrogen Peroxide. By JULIUS WILHELM BRUHL (*Ber.*, 1900, 33, 1709—1710).—The explosive substance previously described (*Abstr.*, 1896, ii, 163) cannot be acetic peroxide as suggested by Nef (*Annalen*, 1897, 298, 290, 327), and again by Bach (*Ber.*, 1900, 33, 1506), since its boiling point is much too high, and its instability is the only point of resemblance. The view that hydrogen peroxide is HO:OH is supported by its high dielectric constant (92.8 at 18°) and by the absence of electrical absorption. T. M. L.

Action of Iodides and of Hydriodic Acid on Sulphur Dioxide. By ARMAND BERG (*Bull. Soc. Chim.*, 1900, [iii], 23, 499—501. Compare this vol., ii, 398).—When aqueous solutions of sulphur dioxide and potassium iodide or hydriodic acid are mixed, a yellow coloration is produced which is probably due to the formation of an unstable compound; it is not caused by free iodine. On keeping, and especially under the influence of light and heat, the yellow colour gradually disappears and one-third of the total sulphur present is deposited, whilst the remaining two-thirds is converted into sulphuric acid. A small quantity of iodide is thus able to bring about the decomposition of a large quantity of sulphur dioxide, without itself undergoing any permanent change. N. L.

Action of Oxidising Agents on Alkali Iodides. By E. PECHARD (*Compt. rend.*, 1900, 130, 1705—1708. Compare Abstr., 1899, ii, 473).—The liberation of iodine from alkali iodides by oxidising agents is probably due to an intermediate formation of periodate. A cold solution of monosodium periodate interacts with iodides in the following manner: $3\text{NaIO}_4 + 2\text{NaI} + 3\text{H}_2\text{O} = \text{NaIO}_3 + 2\text{Na}_2\text{H}_3\text{IO}_4 + \text{I}_2$. The reaction is not instantaneous, the liberation of iodine being still incomplete after an interval of one hour. Moreover, the following reverse action, $\text{Na}_2\text{H}_3\text{IO}_6 + \text{I}_2 = 3\text{NaIO}_3 + \text{NaI} + 3\text{H}_2\text{O}$, occurs when a solution of disodium periodate is left in contact with iodine, the mixture, which at first is alkaline, gradually becoming neutral. The amount of periodate is estimated by means of standard potassium manganate, prepared by treating an alkaline solution of permanganate with potassium iodide (compare Job, *Compt. rend.*, 1899, 128, 1453). The liberation of iodine from an alkali iodide by ozone follows a similar course, periodate is produced and the ratio between the amounts of free and combined iodine corresponds with that required by the first equation. When slightly acidified hydrogen peroxide is added to potassium iodide solution, iodine and oxygen are liberated, and the mixture becomes alkaline; after 24 hours, however, the alkalinity disappears, and the amount of free iodine diminishes perceptibly. These phenomena are explained in the following manner: the peroxide oxidises the iodide and the solution becomes neutral, the action following the course indicated by the first of the equations given; this results in the formation of the alkaline disodium salt in the presence of which hydrogen peroxide decomposes rapidly, and after 24 hours the solution again becomes neutral in accordance with the second equation. G. T. M.

Viscosity of Sulphur at Temperatures above the Point of Maximum Viscosity. By C. MALUS (*Compt. rend.*, 1900, 130, 1708—1710).—The rate of crystallisation of sulphur rendered viscous by heating at 357° for 10 minutes and then maintained for some time at 100° , depends on the rate of cooling and the time of exposure to the latter temperature; it decreases as the latter increases to a minimum value of 5.25 seconds, which is attained after 5 to 6 hours. This limiting value is identical with that obtained for sulphur rendered viscous by heating at 357° for 3 hours, the rate of crystallisation for this modification of sulphur being invariable.

Sulphur maintained for some time either at 100° or 357° passes into the liquid state, but the tendency to regain the viscous condition which is absent from the sulphur heated at 357° persists in that modification which has lost its viscosity at the lower temperature.

G. T. M.

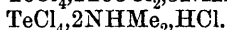
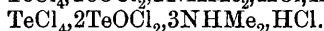
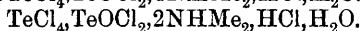
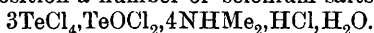
Caro's Reagent. By EUGEN BAMBERGER (*Ber.*, 1900, 33, 1959—1961).—The formula H_2SO_7 is suggested for 'Caro's reagent,' in accordance with Bach's view (this vol., ii, 470) that it is a compound of hydrogen tetroxide and sulphuric acid. On adding a copper salt and then sodium hydroxide to a solution of Caro's reagent, a brownish-black precipitate is produced which is regarded as copper peroxide.

By adding strong sulphuric acid to a cold solution of potassium percarbonate, a solution is obtained which oxidises aniline to nitrosobenzene,

and probably contains the same oxidising agent as a mixture of sulphuric acid with a persulphate or with hydrogen peroxide. T. M. L.

Isomorphism of Selenium and Tellurium. By JAMES F. NORRIS and RICHARD MOMMERS (*Amer. Chem. J.*, 1900, 23, 486—494).—The isomorphism of tellurium with selenium on the one hand, and with platinum on the other hand, has only been established in the case of certain compounds crystallising in the cubic system. Tellurium dimethylamine bromide and selenium dimethylamine bromide are, however, isomorphous, since they both form mixed crystals with tellurium dimethylamine chloride, although none of the crystals have been measured. The corresponding platinum dimethylamine bromide, which belongs to the orthorhombic system, does not form mixed crystals.

The following double salts of tellurium have been prepared, and resemble in composition a number of selenium salts:



Double salts containing tellurium and dimethylamine perbromide could not be prepared. T. M. L.

Combustible Gases of the Atmosphere: Air of Towns. By ARMAND GAUTIER (*Compt. rend.*, 1900, 130, 1677—1684).—The paper contains a detailed account and sketch of the apparatus employed by the author in estimating the amount of hydrogen and carbon present in the atmospheric gases.

The mean of a series of analyses of the atmosphere of Paris, made at different seasons of the year, indicates that this air contains 12.45 mg. of carbon and 3.96 mg. of hydrogen per 100 litres, the quotient C/H being 3.1. Comparative experiments made with purified air containing traces of methane give the quotient C/H as 2.4, indicating that, under these conditions, the hydrogen burns faster than the carbon. It follows from these results that it is still an open question as to whether the combustible gas of the atmosphere consists wholly of methane or of a mixture of this substance with hydrogen and hydrocarbons richer in carbon than the paraffins. G. T. M.

Combustible Gases of the Atmosphere: Air of Forests and High Mountains. By ARMAND GAUTIER (*Compt. rend.*, 1900, 131, 13—18. Compare preceding abstract).—The atmosphere of a forest in July contains only half as much carbon as the air of Paris, whilst the amount of hydrogen is somewhat smaller; the quotient C/H is 2.2, being less than that obtained with air containing traces of methane. Analyses of the air of Mt. Canigou, Pyrenees, indicated a still greater diminution in the amount of carbon, the quotient C/H being only 0.33; the hydrogen present is, therefore, almost entirely uncombined. These results indicate that the hydrocarbons existing in appreciable quantities in the air of towns and woods are, in all probability, emanations from the animals, plants, and humus present in these regions. G. T. M.

Combustible Gases of the Atmosphere: Air of the Sea. Existence of Free Hydrogen in the Terrestrial Atmosphere. By ARMAND GAUTIER (*Compt. rend.*, 1900, 131, 86—90. Compare preceding abstracts).—Examination of the air at the Roches-Douvres lighthouse, 40 kilometres from the coast of France, showed the almost complete absence of hydrocarbons, whilst free hydrogen was present in the proportion of 19.45 c.c. per 100 litres, the same amount as previously found in mountain air. These results confirm the conclusion that air normally contains about 1/5000 of its volume of free hydrogen together with variable quantities of hydrocarbons, the latter being due to the action of vegetable and animal life, to industrial operations, &c.
N. L.

Formation of Nitric Acid during the Combustion of Hydrogen. By MARCELLIN P. E. BERTHELOT (*Compt. rend.*, 1900, 130, 1662—1677. Compare this vol., ii, 474).—When compressed mixtures containing equivalent amounts of hydrogen and oxygen are exploded in the presence of nitrogen, neither ammonia nor nitric acid is produced, a similar result being obtained when the first of these gases is in excess.

When the mixtures contain excess of oxygen, the amount of nitric acid produced increases as the pressure is augmented. Equal volumes of oxygen and hydrogen were exploded in the presence of nitrogen under pressures of 2, 4, and 20 atmospheres; the amounts of nitrogen oxidised were respectively 25, 33, and 45 per cent. by weight of the total hydrogen consumed. When oxygen and hydrogen unite in the oxy-hydrogen blowpipe in an atmosphere of oxygen containing about 7 per cent. of nitrogen, the quantity of nitric acid produced is much smaller than in the preceding experiments. If the partial pressure of the hydrogen is kept constant, whilst the amount of oxygen is gradually increased, the ratio between oxidised and total nitrogen increases to 6.3 per cent. when the mixture contains 1 vol. of hydrogen to 2 vols. of oxygen, and then rapidly diminishes, becoming negligible when the mixture contains 5 vols. of the latter gas.

Experiments made with highly compressed mixtures (8—30 atmospheres) indicate that the yield of nitric acid increases with the pressure, and also to a certain extent with excess of oxygen. When larger quantities of nitrogen are employed, the yield of nitric acid increases considerably, the maximum being attained with the mixture $H_2 : O_2 : N_2 = 1 : 1.7 : 1.3$ under a pressure of 16 atmospheres; further dilution with this gas diminishes its oxidation, a mixture of 1 vol. of hydrogen and 4.5 vols. of air under a pressure of 5.5 atmospheres yielding only a trace of acid. The amount of nitric acid produced during the burning of a feeble jet of hydrogen in air is extremely small.

The paper contains the complete data of each determination of nitric acid, and concludes with a theoretical discussion of the results, which cannot be suitably abstracted.
G. T. M.

Supposed Allotropism of Phosphorus Pentabromide. By J. H. KASTLE and L. O. BEATTY (*Amer. Chem. J.*, 1900, 23, 505—509).—In attempting to determine the transition point from

yellow, rhombic phosphorus pentabromide into the red, prismatic variety, it was found that the latter is probably a perbromide of the formula PBr_7 . Its formation by subliming the yellow pentabromide at 90° is probably due to a partial decomposition into heptabromide and tribromide; phosphorus tribromide reconverts it into the yellow pentabromide. Bromine vapour converts the yellow pentabromide into the red compound, whilst when left in contact with bromine absorbents the reverse change takes place. In contact with water, phosphorus pentabromide gives a colourless solution of phosphoric and hydrobromic acids, whilst the red compound liberates free bromine.

On mixing phosphorus pentabromide and bromine in mol. proportions in a sealed tube and subliming at 90° , bright red, transparent crystals were obtained which gave $P = 5.40$, $Br = 96.20$, the calculated values for PBr_7 being 5.25 and 94.75. T. M. L.

The Lower Oxides of Phosphorus. By ADOLPHE BESSON (*Bull. Soc. Chim.*, 1900, [iii], 23, 582—585).—A criticism of the work of Michaelis and Pitsch (this vol., ii, 137), whose experiments, it is considered, neither justify the conclusions drawn from them nor invalidate the author's previous proofs of the existence of an oxide of phosphorus of the composition P_2O . N. L.

True Atomic Weight of Boron. By GUSTAVUS HINRICHS (*Compt. rend.*, 1900, 130, 1712—1714).—A note on Gautier's determination of the atomic weight of boron (compare this vol., ii, 14, 15). The mean value of this constant calculated by the author's method from Gautier's data is 11.004, that adopted by the latter investigator being 11.016. G. T. M.

Expansion of Fused Silica. By HENRI LE CHATELIER (*Compt. rend.*, 1900, 130, 1703—1705).—Amorphous silica, prepared by fusion in the electric furnace, has between 0° and 1000° a mean coefficient of expansion 0.0000007; this constant is lower than that of any other substance. The melting point of this substance is lowered by the addition of the oxides of the alkali and alkaline earth metals and alumina, but the mixtures have greater coefficients of expansion, the increase being least in the case of the product $10SiO_2, Al_2O_3, 2Li_2O$. G. T. M.

Preparation and Properties of the Silicon Borides SiB_3 and SiB_6 . By HENRI MOISSAN and ALFRED STOCK (*Compt. rend.*, 1900, 131, 139—143).—A mixture of 1 part of boron and 5 parts of crystallised silicon is heated for about 1 minute in a vessel of refractory clay by means of an alternating current of 600 amperes and 45 volts. The cooled mass is treated with a mixture of nitric and hydrofluoric acids in order to remove excess of silicon, and the crystalline portion of the residue after heating with moist potassium hydroxide is extracted with dilute nitric acid and hot water and dried at 130° . The product consists of a mixture of two borides, SiB_3 and SiB_6 , containing about 80—90 per cent. of the latter.

The *hexaboride* is readily oxidised by boiling nitric acid, whereas the *triboride* is only slowly attacked by this reagent; the latter compound,

on the other hand, is decomposed by fused potassium hydroxide, whilst the former remains unchanged.

The triboride forms black, rhombic plates which, when very thin, appear yellowish-brown by transmitted light; its density is 2.52.

The hexaboride is always obtained in thick, black, opaque crystals with somewhat irregular faces; its density is 2.47.

These silicon borides, like the boride and silicide of carbon, are very hard, being intermediate between the diamond and ruby in the scale of hardness; they are soluble in fused silicon and conduct electricity.

When gently heated, they are decomposed by fluorine and are attacked at higher temperatures by chlorine and bromine, but not by iodine or nitrogen. They become superficially oxidised by heating in air or oxygen. They are not affected by the haloid acids, but are slowly decomposed by boiling concentrated sulphuric acid, and rapidly dissolved by fused potassium carbonate or by a mixture of this compound with potassium nitrate; the latter salt alone has no action on them.

G. T. M.

Krypton. By ALBERT LADENBURG and C. KRÜGEL (*Sitzungsber. K. Preuss. Akad. Wiss.*, 1900, 212—217).—The least volatile portion of a large quantity (850 litres) of liquid air was freed from oxygen and nitrogen; the 3.5 litres of gas thus obtained were condensed in a bath of liquid air and under slightly increased pressure; the liquid formed was then allowed to boil, and the gas collected in separate vessels. The greater part came off at -181.2° ; the temperature then rose rapidly to -153° , when the rest of the liquid evaporated; a crystalline residue melted at -147° , and was rapidly vaporised. The first gas (boiling point -181.2°) showed a complete argon spectrum; that obtained from the crystalline residue showed a bright krypton spectrum, and careful investigation pointed to the absence of argon. The density of this krypton was found to be 58.81, and subsequent sparking with oxygen did not alter this value appreciably. The authors suggest that the new atmospheric elements should be placed before Group I of the periodic system, thus: He = 4 before lithium, Ne = 20 before sodium, A = 39 before potassium, and Kr = 59 before copper.

J. C. P.

Sodium and Potassium Amalgams. By ANTOINE GUNTZ and JULES FÉRÉE (*Compt. rend.*, 1900, 131, 182—184).—The solution obtained by adding a mixture of sodium and mercury containing 3.5 per cent. of the former to the fused amalgam Hg_6K at 200° , deposits prismatic needles of the amalgam Hg_5K on cooling to 140° ; the mother liquor solidifies at 96° , and consists of the substance Hg_6K . When either of these substances is submitted to a pressure of 200—1200 kilos. per sq. cm., a saturated solution of sodium in mercury is expressed, and the residue consists of a new amalgam, Hg_4Na .

The ordinary potassium amalgam, Hg_{12}K , when compressed, is converted into a new amalgam, Hg_{10}K . A solution of potassium in mercury, when cooled to -19° , yields crystals of another potassium amalgam, Hg_{18}K ; this substance, on warming, yields crystals of Hg_{12}K and a saturated solution of potassium in mercury.

G. T. M.

Impossibility of the Direct Formation of Potassium Chlorate by Electrolysis. By ANDRE BROCHET (*Compt. rend.*, 1900, 130, 1624—1627).—When a solution of potassium chloride mixed with potassium hydroxide is electrolysed in presence of finely divided cobalt oxide, practically no chlorate is formed, and since the chlorate is not decomposed by cobalt oxide, the author regards this result as conclusive proof that the chlorate produced by electrolysis is always a secondary product from the hypochlorite, and is never a primary product, even in a solution so strongly alkaline that the intermediate formation of hypochlorite cannot be detected by analysis.

C. H. B.

Compound of Silver Fluoride with Ammonium Fluoride. By BRUNO GRUTZNER (*Arch. Pharm.*, 1900, 238, 1—3. Compare von Helmolt, *Abstr.*, 1893, ii, 373).—By dissolving moist, freshly precipitated silver oxide in cold concentrated aqueous ammonium fluoride, and cooling with ice, a small quantity of a double salt, $2\text{NH}_4\text{F} \cdot \text{AgF} \cdot \text{H}_2\text{O}$, was obtained; this compound is not hygroscopic.

C. F. B.

Physicochemical Relations of Aragonite and Calcite. By H. W. FOOTE (*Zeit. physikal. Chem.*, 1900, 33, 740—759).—From experiments on the decomposition of aragonite and calcite by potassium oxalate, and on the conductivity of solutions of these two in water saturated with carbon dioxide, the author concludes that at the ordinary temperature calcite is more stable than aragonite, although the solubility curves deduced from the conductivity experiments approach each other with rising temperature. It seems probable, from the results obtained by the author and others, that under atmospheric pressure calcite remains the more stable form up to its melting point. The transformation of aragonite into calcite is accompanied by a slight evolution of heat.

J. C. P.

Formation of Marine Anhydrite. By HEINRICH VATER (*Sitzungsber. K. Preuss. Akad. Wiss.*, 1900, 269—294).—After reviewing the work done by others on the formation of anhydrite, the author describes experiments showing that at the ordinary temperature calcium sulphate crystallises from a saturated sodium chloride solution as gypsum and not as anhydrite; this holds also when the sodium chloride solution contains 3 per cent. of magnesium chloride. From saturated magnesium chloride solutions, calcium sulphate crystallises as gypsum at the ordinary temperature, and as the compound $2\text{CaSO}_4 \cdot \text{H}_2\text{O}$ at 40° .

J. C. P.

Solubility of Tricalcium Phosphate in Natural Waters in the Presence of Carbonic Acid. By TH. SCHLÖESING (*Compt. rend.*, 1900, 131, 149—153).—Hydrated tricalcium phosphate, $\text{Ca}_3(\text{PO}_4)_2 \cdot \text{H}_2\text{O}$, prepared by neutralising an aqueous solution of phosphoric acid with calcium hydroxide, is almost insoluble in distilled water at the ordinary temperature; it dissolves to a far greater extent in solutions of carbonic acid, but is much less soluble in water containing this acid together with an amount of calcium hydrogen carbonate corresponding with the pressure of the dissolved carbon dioxide. Since the latter condition usually obtains in surface waters, it follows that the carbon

dioxide present exerts but little solvent action on the calcium phosphate present in artificial manures.

The paper contains two tables showing the solubility of the phosphate in carbonic acid and calcium hydrogen carbonate solutions of varying strengths. G. T. M.

Influence of Temperature and Concentration on the Saline Constituents of Boiler Water. By CECIL H. CRIBB (*Analyst*, 1900, 25, 169—183).—The author communicates the analyses of a large number of boiler waters before and after boiling at different pressures and for different periods; the results are given in eleven tables.

Magnesium chloride, which is not decomposed by mere boiling with water, decomposes, however, at a higher temperature, and deposits magnesium hydroxide or even oxide. Calcium sulphate is not rendered insoluble at 150°, as has been stated.

Many obscure points have been noticed which require investigation before a clear idea is obtained as to what really takes place with the dissolved salts when waters are heated under pressure. L. DE K.

Solubility of Cupric Chloride in Organic Media. By WILLIAM ECHSNER DE CONINCK (*Compt. rend.*, 1900, 131, 58—60).—A qualitative and quantitative study of the solubility of anhydrous and hydrated cupric chloride in a variety of organic liquids.

G. T. M.

Copper Carbonate. By MAX GROGER (*Zeit. anorg. Chem.*, 1900, 24, 127—138).—The greenish-blue precipitate obtained by precipitating a solution of sodium carbonate with copper sulphate at the ordinary temperature is colloidal, and contains more or less absorbed sodium carbonate; when equivalent quantities of the two solutions are employed, the copper carbonate contains cupric oxide and carbon dioxide in the ratio $\text{CuO} : \text{CO}_2 = 2 : 1$. The amount of carbon dioxide in the precipitate decreases with the increase of excess of sodium carbonate, and with excess of copper sulphate the precipitate contains basic copper sulphates. The amount of water in the precipitate is variable, as is the case with all colloids. When the precipitate is allowed to remain in contact with the mother liquor, it becomes crystalline, and then has the composition expressed by the formula $6\text{CuO}, 3\text{CO}_2, 4\text{H}_2\text{O}$; this change takes place more slowly as the excess of sodium carbonate increases, and with a large excess of sodium carbonate blue crystals of sodium copper carbonate, $\text{Na}_2\text{CO}_3, \text{CuCO}_3, 3\text{H}_2\text{O}$, are formed together with a small quantity of a dark brown copper carbonate.

The precipitate obtained from sodium hydrogen carbonate and copper sulphate at low temperatures is also colloidal, contains absorbed sodium hydrogen carbonate, has the ratio $\text{CuO} : \text{CO}_2 = 8 : 5$, and is not altered by drying at the ordinary temperature. When dried over sulphuric acid, it has the composition $8\text{CuO}, 5\text{CO}_2, 7\text{H}_2\text{O}$. When precipitated in the presence of excess of copper sulphate, it contains basic copper sulphates, and when allowed to remain in contact with the mother liquor is gradually converted into the crystalline com-

pound $6\text{CuO}, 3\text{CO}_2, 4\text{H}_2\text{O}$. An excess of sodium hydrogen carbonate accelerates the change. E. C. R.

Distillation of Amalgams and the Purification of Mercury. By GEORGE A. HULETT (*Zeit. physikal. Chem.*, 1900, 33, 611—621).—The purity of mercury may be very accurately found by E.M.F. determinations; thus the E.M.F. of the chain $\text{Zn electrolyte} \mid \text{Hg}$ is very greatly altered by the addition of small quantities of zinc to the mercury. Mercury may be conveniently distilled by means of an ordinary distilling flask fitted to an exhaust pump, as for the distillation of other liquids under reduced pressure, if a capillary tube be passed down into the mercury so that a fine stream of air or nitrogen passes through the metal during the distillation. Contrary to general statements, mercury is completely freed from zinc and cadmium by distillation, these metals not distilling over so long as the surface is bright. If, however, a film of oxide forms on the surface, some of this may be mechanically carried over. Determinations of the zinc indicate that at 210° the vapour tension of mercury is at least 3×10^7 times that of zinc. L. M. J.

Decomposition of Metallic Chlorides. By WILLIAM ECHSNER DE CONINCK (*Compt. rend.*, 1900, 130, 1627—1628).—When a dilute aqueous solution of mercuric chloride is filtered through animal charcoal, the salt is absorbed somewhat rapidly, but not completely, and it may be regarded as stable unless exposed to a very bright light. Cadmium chloride and aluminium chloride are somewhat slowly absorbed, and may be regarded as very stable, but stannic chloride, like the stannous salt, is rapidly decomposed with formation of an oxychloride. The rapid alteration of the stannous and stannic salts seems to show that the charcoal exerts an oxidising action. With ferric chloride solution, the charcoal seems to act as a dialyser, the whole of the iron being removed whilst the chlorine remains in solution. C. H. B.

Direct Formation of Crystallised Mercuric and Mercurous Iodides. By F. BODROUX (*Compt. rend.*, 1900, 130, 1622—1624).—If a somewhat concentrated aqueous solution of a mercuric salt, preferably the acetate, is mixed with a small quantity of methyl iodide and allowed to remain at the ordinary temperature, mercuric iodide gradually separates in red lamellæ as much as 10 mm. in breadth. Some of the first crystals are yellow, but gradually change to red. Other alkyl iodides behave similarly, but the yield is not so good.

Mercurous iodide can be obtained abundantly in yellow, lustrous plates by adding ethyl or methyl iodide to a cold saturated solution of mercurous nitrate. C. H. B.

Mercury Antimonide. By ALFRED PARTHEIL and E. MANNHEIM (*Arch. Pharm.*, 1900, 238, 166—184).—See this vol., i, 479.

Mercury Phosphide and Phosphonium Compounds. By ALFRED PARTHEIL [with A. VAN HAAREN] (*Arch. Pharm.*, 1900, 238, 28—42).—When hydrogen phosphide, prepared from sodium hypo-

phosphite, zinc, and hydrochloric acid, and therefore mixed with much hydrogen, is passed through dilute alcoholic mercuric chloride, a yellow precipitate of $\text{PHg}_2\text{Cl}, \text{HgCl}_2, 1\frac{1}{2}\text{H}_2\text{O}$ is obtained. When comparatively pure hydrogen phosphide, prepared from zinc phosphide and hydrochloric acid, is passed into a $2\frac{1}{2}$ per cent. solution of mercuric chloride in alcohol, a dark brown precipitate is obtained eventually, almost free from chlorine, but having approximately the composition $\text{P}_2\text{Hg}_5\text{O}_4$; this is unstable and readily evolves hydrogen phosphide. When hydrogen phosphide is passed over dry mercuric chloride, the hydrogen chloride liberated does not correspond with the formation of P_2Hg_3 .

Mercury phosphide, P_2Hg_3 , was prepared eventually, as a brown powder, by Granger's method (Abstr., 1892, 1398), and heated with ethyl iodide at 160° for 4—5 hours; in addition to mercuric iodide, a yellow *tetraphosphonium mercuriodide*, $\text{PEt}_4\text{I}, 2\text{HgI}_2$, was obtained. By digesting this in alcoholic solution with silver oxide, and evaporating the alkaline filtrate, a crystalline mass, doubtless of *tetraphosphonium hydroxide*, was obtained; from this, the crystalline, hygroscopic *chloride* was prepared by neutralisation with hydrochloric acid. The *mercurichloride*, $\text{PEt}_4\text{Cl}, 2\text{HgCl}_2$, *aurichloride*, $\text{PEt}_4\text{Cl}, \text{AuCl}_3$, melting at 179° , and *platinichloride*, $2\text{PEt}_4\text{Cl}, \text{PtCl}_4$, were also prepared. Some of these compounds were also prepared, for the sake of comparison, from triethylphosphine; the products were identical with those described already. The precipitate obtained by mixing tetraphosphonium iodide and mercuric iodide in alcoholic solution at the ordinary temperature has the composition $2\text{PEt}_4\text{I}, \text{HgI}_2$, but it is converted into the compound described above when it is heated at 160° with mercuric iodide and ethyl iodide.

By heating mercury phosphide with methyl iodide at 140 — 150° , some analogous compounds were obtained. *Tetramethylphosphonium mercuriodide*, $\text{PMe}_4\text{I}, 2\text{HgI}_2$, melting at 172° ; *mercurichloride*, $\text{PMe}_4\text{Cl}, \text{HgCl}_2$, melting at 249° ; *platinochloride*, $2\text{PMe}_4\text{Cl}, \text{PtCl}_4$, and *aurichloride*, $\text{PMe}_4\text{Cl}, \text{AuCl}_3$, were prepared. C. F. B.

Ceric Sulphates. By WILHELM MUTHMANN and L. STÜTZEL (Ber., 1900, 33, 1763—1765).—When ceric oxide is dissolved in concentrated sulphuric acid and the solution evaporated, a yellow salt is first obtained, which is normal ceric sulphate, $\text{Ce}(\text{SO}_4)_2, 4\text{H}_2\text{O}$. The mother liquors often, but not always, yield a second salt, forming large, reddish-brown crystals, which are readily decomposed by water, with formation of insoluble basic substances. This substance has the composition $\text{Ce}_2(\text{SO}_4)_3, 2\text{Ce}(\text{SO}_4)_2, 20\text{H}_2\text{O}$, and is the only ceric sulphate which could be obtained in addition to the normal salt. A. H.

Luminescence Spectra. By WILHELM MUTHMANN and E. BAUR (Ber., 1900, 33, 1748—1763).—The authors regard the luminescence spectra yielded by certain of the rare earths as of considerable value for their identification, in spite of the fact that these spectra are much affected by the presence of small quantities of other substances, such as lime, gypsum, &c. Detailed measurements and diagrams are given for lanthanum oxide, yttrium oxide, yttrium sulphates of various origins, and oxides and sulphates obtained from monazite and commercial thorium nitrate. The spectra of the yttrium sulphates, and of

the oxides and sulphates derived from monazite and thorium nitrate, are essentially made up of lines due to yttria and gadolinia, to the latter of which the authors ascribe four bands. By fractionation of a crude yttrium earth by ammonia, and crystallisation of the formate, each operation being repeated 50 times, an earth containing very little erbia is obtained, which shows strong lines of yttria and gadolinia. When this material is divided into about 20 fractions by means of potassium dichromate, the last of these contains only traces of erbia and very little gadolinia. Further fractionation with ammonia removes the remainder of the erbia, whilst the gadolinia accumulates in the last fractions. Thoria itself gives no luminescence spectrum, the spectra actually observed with the oxides and sulphates derived from monazite and commercial thorium nitrate being due to yttria and gadolinia.

The authors have not observed the independent disappearance of the single bands of the yttria and gadolinia spectra in the manner described by Crookes (*Trans.*, 1889, 55, 270), whilst, on the other hand, Crookes has not described spectra corresponding with those ascribed by the authors to almost pure yttria and gadolinia respectively.

A. H.

Natural and Artificial Pozzuolana. By GIOVANNI GIORGIS and UGO ALVISI (*Gazzetta*, 1900, 30, i, 436—508. Compare this vol., ii, 348).—A discussion is given of the literature of the setting of hydraulic materials, followed by a bibliography of the subject.

T. H. P.

Chemical Constitution of Steels; Influence of Tempering on the State of Combination of Elements other than Carbon. By ADOLPHE CARNOT and GOUTAL (*Compt. rend.*, 1900, 131, 92—96. Compare *Abstr.*, 1897, ii, 520, 555).—It has been shown (*Abstr.*, 1897, ii, 555) that in slowly cooled steel, the sulphur present combines with the manganese in preference to iron, since treatment with cupric potassium chloride solution leaves an insoluble residue of cupric sulphide containing sulphur equivalent to the manganese present, whereas iron sulphide is not attacked by the solvent in question. Precisely similar results are obtained with tempered steel, whence it follows that tempering has no influence on the condition in which sulphur exists in the metal. The same applies to phosphorus, present as iron phosphide, Fe_3P , which is left undissolved when the tempered or untempered steel is treated with cupric potassium chloride solution. On the other hand, arsenic, which exists in the free state in untempered steel, is found to be present mainly as an iron arsenide, Fe_2As , in the tempered metal, this arsenide being left undissolved by treatment with 7 per cent. sulphuric acid with exclusion of air. Copper is present chiefly in the uncombined state in both tempered and untempered steel, as was shown microscopically after digestion with dilute acid or with a mixture of hydrogen peroxide and ammonium chloride solution. Nickel in tempered, as in untempered, steel appears to exist in the metallic condition, either mixed with or dissolved in the iron.

N. L.

Iron Selenides. By HENRI FONZES-DIACON (*Compt. rend.*, 1900, 130, 1710—1712).—The combination of iron and selenium at high temperatures always gives rise to compounds containing an excess of selenium over that indicated in the formula FeSe . Amorphous products only are obtained by the action of hydrogen selenide or selenium vapour on red hot iron. Ferric selenide, Fe_2Se_3 , produced by the action of hydrogen selenide on ferric oxide heated to bright redness, forms a grey, microcrystalline powder with a blue reflex.

The selenides, Fe_3S_4 and Fe_7S_8 , are obtained in a similar manner from the peroxide or anhydrous ferric chloride at somewhat higher temperatures; these compounds are crystalline, and belong apparently to the cubic system.

Iron diselenide, FeSe_2 , prepared in a similar manner at a dull red heat, forms pseudomorphs after crystallised anhydrous ferric chloride; when heated in a current of oxygen, it is oxidised to ferric oxide and selenium dioxide.

The higher selenides are all converted into the monoselenide by reduction with hydrogen; the subselenide, Fe_2Se , however, could not be obtained by this process. When the monoselenide is heated in the electric furnace, a portion undergoes complete dissociation, whilst the residue remains unaltered. The stability of the selenides towards hydrogen chloride or a concentrated solution of this gas increases with the percentage amount of selenium, the diselenide not being attacked. The selenium in these compounds is readily replaced by chlorine, and fuming nitric acid converts them into selenites. G. T. M.

Behaviour of Potassium Cobaltocyanide and of Chromous Compounds towards Oxygen Gas. By WILHELM MANCHOT and JOHANNES HERZOG (*Ber.*, 1900, 33, 1742—1748).—When a solution of potassium cobaltocyanide is rapidly oxidised by atmospheric oxygen, it is found that twice as much oxygen is absorbed as is necessary for the conversion of the cobalto- into the cobalti-cyanide, according to the equation $2\text{K}_4\text{CoCy}_6 + \text{H}_2\text{O} + \text{O} = 2\text{K}_3\text{CoCy}_6 + 2\text{KOH}$.

At the close of the reaction, moreover, the whole of the oxygen absorbed is found to be present in the form of hydrogen peroxide. On the other hand, when the oxidation is carried out slowly, the oxygen absorbed is only slightly in excess of that required by the equation, and a correspondingly small amount of hydrogen peroxide is present. This is due to the fact that in the first case the direct oxidation proceeds so rapidly that the slower, indirect oxidation by means of hydrogen peroxide does not occur to an appreciable extent, whilst in the second case this factor becomes of importance. When a solution of potassium cobaltocyanide, prepared by adding potassium cyanide solution to a well boiled solution of cobalt sulphate, is simply boiled, hydrogen is evolved, the volume of which is equal to that of the oxygen absorbed during the rapid oxidation by air, and is chemically equivalent to the oxygen required according to the foregoing equation.

Solutions of chromous salts also evolve hydrogen when they are boiled or treated with platinised platinum, but no hydrogen peroxide is formed during their oxidation by atmospheric oxygen, and the amount of oxygen absorbed is simply that required for the oxidation.

The author therefore regards the oxidation of the chromous salts as due to the direct action of the oxygen of the air, whilst that of potassium cobaltocyanide is a spontaneous oxidation effected by the oxygen of the water present, the function of the absorbed oxygen being to unite with the liberated hydrogen, and thus destroy the equilibrium which normally exists between the cobaltocyanide, hydrogen, and cobaltocyanide.

A. H.

Ammonium Chromous Sulphate. By CHARLES LAURENT (*Compt. rend.*, 1900, 131, 111—113).—*Ammonium chromous sulphate*, $(\text{NH}_4)_2\text{Cr}(\text{SO}_4)_2 + 6\text{H}_2\text{O}$, prepared by concentrating in an atmosphere of carbon dioxide an aqueous solution of ammonium and chromous sulphates in molecular proportion, forms large, blue crystals resembling those of the double sulphates of the magnesium series. It is insoluble in alcohol, but readily soluble in water; 100 c.c. of the saturated aqueous solution at 20° contain 55 grams of the salt. When exposed to air, it is rapidly oxidised and converted into chromic salt.

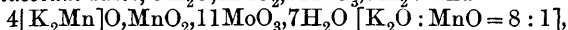
N. L.

Permanganomolybdates. By CARL FRIEDHEIM and MINNA SAMELSON (*Zeit. anorg. Chem.*, 1900, 24, 65—107).—The authors have repeated the work of Rosenheim and Itzig (*Abstr.*, 1898, [ii, 154], Struve (*J. pr. Chem.*, 1854, 61, 449), and Péchard (*Abstr.*, 1897, ii, 498), and have prepared the following compounds.

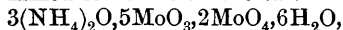
Ammonium permanganomolybdate, $3(\text{NH}_4)_2\text{O}, \text{MnO}_2, 9\text{MoO}_3, 7\text{H}_2\text{O}$, is obtained by adding 1·8 litres of a concentrated solution of ammonium paramolybdate (1 litre = 250 grams) to 100 c.c. of a solution of manganous chloride (1 litre = 875 grams) and then 800 c.c. of 2·5 per cent. hydrogen peroxide; the mixture is boiled for some time and filtered, when on cooling the salt separates in small, lustrous, red rhombohedra. It is necessary to employ solutions of the above strength, for under other conditions different salts are formed. The isomorphous mixture $4[(\text{NH}_4)_2\text{Mn}]_2\text{O}, \text{MnO}_2, 11\text{MoO}_3, 8\text{H}_2\text{O}$ [$(\text{NH}_4)_2\text{O} : \text{MnO} = 8 : 1$] is obtained by employing 20 per cent. more of a 3 per cent. solution of hydrogen peroxide in the above reaction. The salt, $2(\text{NH}_4)_2\text{O}, \text{MnO}_2, 7\text{MoO}_3, 5\text{H}_2\text{O}$, is obtained by employing 18·5 per cent. solution of hydrogen peroxide in the above reaction.

The isomorphous mixture $4[(\text{NH}_4)_2\text{Mn}]_2\text{O}, \text{MnO}_2, 10\text{MoO}_3, 6\text{H}_2\text{O}$ [$(\text{NH}_4)_2\text{O} : \text{MnO} = 17 : 3$] is obtained by boiling a solution of the salt $3(\text{NH}_4)_2\text{O}, 5\text{MoO}_3, 2\text{MoO}_4, 6\text{H}_2\text{O}$ with the equivalent quantity of manganous chloride. It crystallises in lustrous, red rhombohedra.

The *potassium* salts, $3\text{K}_2\text{O}, \text{MnO}_2, 8\text{MoO}_3, 3\text{H}_2\text{O}$ and



are obtained in a similar manner by the action of hydrogen peroxide on mixed solutions of potassium paramolybdate and manganous chloride. *Potassium permanganomolybdate*, $3\text{K}_2\text{O}, \text{MnO}_2, 9\text{MoO}_3, 5\text{H}_2\text{O}$, corresponding with the above ammonium salt, is obtained by adding a saturated solution of potassium chloride to the corresponding ammonium salt, or the salt $4(\text{NH}_4)_2\text{O}, \text{MnO}_2, 10\text{MoO}_3, 6\text{H}_2\text{O}$. The isomorphous mixture $3[\text{K}_2(\text{NH}_4)_2]_2\text{O}, \text{MnO}_2, 8\text{MoO}_3, 4\text{H}_2\text{O}$ [$\text{K}_2\text{O} : (\text{NH}_4)_2\text{O} = 4 : 1$] is obtained by boiling mixed solutions of the salt



manganous chloride, and potassium chloride, and is a microcrystalline, orange-red powder.

A repetition of Struve's work resulted in the preparation of the following new salts. *Potassium manganese permanganomolybdate*, $2K_2O, MnO, MnO_2, 9MoO_3, 8H_2O$, is obtained by treating a solution of potassium trimolybdate and manganous sulphate with chlorine. *Ammonium permanganomolybdate*, $4(NH_4)_2O, MnO_2, 11MoO_3, 7H_2O$, is obtained in small quantities by prolonged boiling of pure hydrated manganese dioxide with a solution of ammonium paramolybdate. The salt, $3(NH_4)_2O, MnO_2, 9MoO_3, 8H_2O$, is obtained when hydrated manganese dioxide containing manganous oxide is employed in the preparation of the preceding salt.

A repetition of Péchard's and Rosenheim and Itzig's work resulted in the preparation of the following salts. The isomorphous mixture $3[K_2(NH_4)_2Mn]O, MnO_2, 10MoO_3, 6H_2O$ [$K_2 : (NH_4)_2 : Mn = 2 : 20 : 5$] is obtained by the action of potassium permanganate on a mixture of ammonium paramolybdate and manganous chloride, and crystallises in lustrous, red rhombohedra. The mixture,

$3[(NH_4)_2Mn]O, MnO_2, 10MoO_3, 10H_2O$ [$(NH_4)_2 : Mn = 10 : 3$], obtained by the action of potassium permanganate on ammonium manganese molybdate, crystallises in beautiful, red rhombohedra. If the crystallisation of the preceding mixture is effected rapidly, it contains potassium salt in the proportion $(NH_4)_2 : K : Mn = 12 : 1 : 1$. The isomorphous mixture $4[K_2(NH_4)_2Mn]O, MnO_2, 10MoO_3, 5H_2O$ [$(NH_4)_2 : K_2 : Mn = 20 : 5 : 1$] is obtained by reducing a boiling solution of potassium permanganate and ammonium molybdate with alcohol until the violet colour is changed to red. When excess of ammonium molybdate is employed, the salt $3[(NH_4)_2Mn]O, MnO_2, 10MoO_3, 8H_2O$ [$(NH_4)_2 : Mn = 20 : 1$] is formed.

The salts described above form a new series of compounds as shown by the formula $2R_2O, MnO_2, 7MoO_3$; $3R_2O, MnO_2, 8MoO_3$; $3R_2O, MnO_2, 9MoO_3$; $3R_2O, MnO_2, 10MoO_3$; $4R_2O, MnO_2, 10MoO_3$; $4RO_2, MnO_2, 11MoO_3$.
E. C. R.

Reduction of Tungsten Trioxide by Zinc. Preparation of Pure Tungsten. By MARCEL DELÉPINE (*Compt. rend.*, 1900, 131, 184—187. Compare this vol., ii, 8).—Tungsten is readily prepared by heating a mixture of tungsten trioxide or ammonium tungstate with powdered zinc in a gas or coke furnace. A product containing 94 per cent. of the element may be obtained from commercial zinc and crude tungsten trioxide, and the percentage is raised to 99.9 by extracting the substance with sodium hydroxide solution and drying the residue at red heat in a current of hydrogen. The metal is produced by this process in the form of a grey, crystalline powder which assumes a metallic lustre on compression or trituration; its density is 18.64, corresponding closely with the value obtained for the massive form. The heat of combustion of the metal to the trioxide is 196.44 Cal. at constant vol. and 197.3 Cal. at constant pressure; the heats of oxidation of WO_2 to WO_3 and W to WO_2 at constant pressure are 64.9 and 132.4 Cals. respectively.

Tungsten trioxide may be readily reduced by hydrogen at temperatures below the fusing point of glass. G. T. M.

Crystallisation of Gold. By ALFRED DITTE (*Compt. rend.*, 1900, 131, 143—149).—When a sheet of gold is heated for several hours in contact with a mixture of sodium chloride and sodium pyrosulphate, the surface of the metal becomes eroded by the action of the pyrosulphuryl chloride produced, and the gold chloride which results subsequently dissociates, leaving this element in a crystalline form. The same result is obtained by employing a mixture of ferrous sulphate and sodium chloride, and although the temperature attained is below the melting point of gold, the metal produced from the chloride is found in the form of rhombic plates, small prisms, six-rayed rosettes, and fern-like aggregates; a portion is also obtained in non-crystalline filaments indicating incipient fusion. These appearances resemble those presented by the gold of auriferous minerals. When quartz fragments are introduced with the mixtures employed in the preceding experiments, it is found that the gold crystals and filaments are deposited at the surface and in the fissures of the mineral.

The aqueous extract of the salts after fusion contains sodium sulphide, produced by the action of the oxides of sulphur on the fused sodium chloride; when the oxides of iron or other metals are present, the corresponding sulphides are produced by double decomposition. These reactions are comparable with those occurring in nature and explain the presence of the sulphides in auriferous quartz.

A mixture of sodium chloride and pyrosulphate attacks platinum in a similar manner, the fused mass containing detached particles of the metal and traces of its chlorides. G. T. M.

Gold-Aluminium Alloys. By CHARLES T. HEYCOCK and FRANCIS H. NEVILLE (*Phil. Trans.*, 1900, A., 194, 201—232).—Addition of aluminium to gold lowers the freezing point of the latter metal, and an alloy containing 21.5 atomic per cent. of aluminium freezes as low as 525°. Further addition of aluminium raises the freezing point until a maximum is reached at 625°, corresponding with an alloy of the composition Au_2Al . The freezing point curve then falls again, reaching another minimum or eutectic point at about 570°, corresponding with 40 atomic per cent. of aluminium. From that point, the curve rises rapidly to 1060°, the freezing point of the alloy AuAl_2 , the purple compound discovered by Sir W. Roberts-Austen. After passing this maximum, the curve falls again and has a minimum close to the freezing point of pure aluminium. This curve, on which a large number of points have been determined, shows the existence of the compounds Au_2Al and AuAl_2 , whilst other singularities, less well marked than those mentioned, point to the formation at various stages of less stable compounds, probably Au_4Al , Au_5Al_2 (or Au_5Al_3), and AuAl . As the curve is followed, the different substances that crystallise out may be traced in the changing colour of the alloys, which are at first yellow, owing to the presence of free gold, then white, then purple, and finally white again as the aluminium end of the curve is reached.

These results are fully borne out by a microscopic study of the

alloys. In particular, the alloys which are approximately of the composition Au_2Al and AuAl_2 show the structure which is characteristic of a nearly pure substance; polygonal sections of the crystals cover the surface, divided only by fine boundary lines; as the composition of the alloy departs from that of the pure compound, so these boundary lines increase in size. The results given by slowly cooled alloys are the same in kind as those obtained from quickly cooled alloys. A number of photomicrographs illustrate this part of the paper.

J. C. P.

Mineralogical Chemistry.

Ankerite from Missouri. By AUSTIN F. ROGERS (*Kansas Univ. Quart.*, 1899, 8, A, 183).—The material analysed consists of salmon coloured, crystalline masses, with minute crystals lining crevices; it occurs with hæmatite, chalybite, calcite, and amethyst, near Rolla, Phelps Co. The formula agrees closely with that for normal ankerite, namely, $2\text{CaCO}_3, \text{MgCO}_3, \text{FeCO}_3$:

CaO.	MgO.	FeO.	CO ₂ .	Total.	Sp. gr.
28·41	10·20	17·22	44·21	100·04	2·99
					L. J. S.

Origin of Nitrates in Cavern Earths. By WILLIAM H. HESS (*J. Geol.*, 1900, 8, 129—134. Compare Abstr., 1896, ii, 529).—The considerable deposits of nitrates in the great limestone caves of Virginia, Kentucky, and Indiana are often supposed to have been formed by bats; but this, it is pointed out, is probably incorrect. The author supposes that the nitrates in the surface soil have been carried by percolating water (surface drainage) into the caves below, where, in cases in which evaporation exceeds inflow, the nitrates are deposited. In support of this theory are given analyses of cave earth, bat guano, and of the water which drips from the roof of the Mammoth Cave, Kentucky. The same explanation would also apply to the deposits of nitrates found under rock ledges. L. J. S.

Composition of Sulphohalite. By SAMUEL L. PENFIELD (*Amer. J. Sci.*, 1900, [iv], 9, 425—428).—From the single partial analysis that has been made of sulphohalite, the formula was deduced as $3\text{Na}_2\text{SO}_4, 2\text{NaCl}$ (Abstr., 1889, 217). Recent attempts by de Schulten and by van't Hoff and Saunders to prepare this compound artificially have failed, and the existence of sulphohalite has consequently been doubted; a new analysis was therefore desirable. The following are the new results obtained with carefully purified material from a portion of the same optically isotropic, rhombic dodecahedral crystal used for the previous analysis:

SO ₃ .	Na ₂ O.	K ₂ O.	Na.	Cl.	F.	Ignition.	Total.	Sp. gr.
41·79	32·37	0·10	11·60	9·10	4·71	0·15	99·82	2·500

This gives the formula $2\text{Na}_2\text{SO}_4, \text{NaCl}, \text{NaF}$. The presence of fluorine is unexpected, but may be explained by the borax deposits of Borax Lake, San Bernardino Co., California, having been formed by fumerole action. Sulphohalite is intimately associated with hanksite, a mineral also containing three acid constituents, $9\text{Na}_2\text{SO}_4, 2\text{Na}_2\text{CO}_3, \text{KCl}$, (Abstr., 1897, ii, 49).

L. J. S.

Melilite Group of Minerals. By FERDINAND FOUQUE (*Bull. Soc. franç. Min.*, 1900, 23, 10—15).—In the analysis of silicate rocks by Deville's method, in which the material is fused with lime, it is found that the fused mass on cooling sometimes consists almost entirely of a crystalline mass of a mineral of the melilite group. Thin sections under the microscope show tetragonal crystals which are sometimes arranged in spherulitic groups 1 mm. in diameter; the crystals are always optically positive with marked birefringence, but are often nearly isotropic in the centre. Analyses I and II are of the products obtained by fusing an andesite and a basalt respectively with about an equal amount of calcium carbonate.

	TiO ₂ .	SiO ₂ .	Al ₂ O ₃ .	Fe ₂ O ₃ .	FeO.	CaO.	MgO.	Na ₂ O.	K ₂ O.	Total.	Sp. gr.
I.	0.23	36.47	13.00	2.22	2.93	42.18	0.89	2.44	0.46	100.82	2.95
II.	0.56	32.55	12.49	1.48	4.67	42.03	3.86	2.35	0.63	100.62	2.99

Vogt has considered the members of the melilite group to consist of mixtures of the two end members gehlenite and the non-aluminous åkermanite, which are optically negative and positive respectively. According to this theory, a member with 12 per cent. of alumina should be optically negative and almost isotropic, but this is opposed to the present observations.

L. J. S.

Gadolinite from Batum. By G. P. TCHERNIK (*J. Russ. Phys. Chem. Soc.*, 1900, 32, 252—266).—Gadolinite occurring in the form of a cement occurs with flesh-red feldspar in a coarse-grained granite from the bed of the river Chorok. The mineral, which has a hardness slightly less than 7 and a sp. gr. 4.205, shows no cleavage, the fracture being conchoidal. It has a dark resiny-black colour with a distinct greenish shade and a fatty lustre, and is opaque even at the edges of very thin fragments; from external examination, it appears to be amorphous. It does not melt in the blowpipe flame, but readily breaks up and increases slightly in volume; on cooling, it becomes greyish-green in colour. Concentrated hydrochloric acid and aqua regia readily attack, but do not completely decompose it, whilst sulphuric acid acts less energetically. Analysis:

Y ₂ O ₃ .	Er ₂ O ₃ .	CaO.	FeO.	BeO.	Nb ₂ O ₅ .	TiO ₂ .	CeO.
28.38	11.01	0.53	10.02	4.22	1.05	5.08	4.92
	LaO.	DiO.	SiO ₂ .	H ₂ O.	Total		
	4.86	4.99	22.20	0.73	98.87		

with traces of MgO, MnO, Al₂O₃, K₂O, Na₂O and P₂O₅. The Nb₂O₅, which is probably due to the presence of some other mineral, possibly contains small quantities of Ta₂O₅.

T. H. P.

Manganocalcite and Angolite. By EDUARD BREUSING (*Inaug. Diss. and Jahrb. Min.*, 1900, Beil.-Bd., 13, 265—330).—Mangano-

calcite from Schemnitz, Hungary, was described by Breithaupt as an orthorhombic carbonate of manganese, calcium, &c., belonging to the aragonite group. It was afterwards shown by Des Cloizeaux (Abstr., 1886, 320) to be a mixture of carbonate and an anorthic hydrated silicate of manganese, and this is confirmed by the present author, who gives the name angolite (angolith) to the latter. The angolite can only be separated from the mixture by mechanical means, since it is readily decomposed by acids; it is flesh-red to rose-coloured, with a vitreous lustre; $H = 5$; sp. gr. 3.054—3.067; there is a cleavage parallel to the length of the fibres, and the pure material contains no carbon dioxide, calcium or magnesium. The mixture occurs in globular aggregations with a radial structure, and it varies considerably in composition; the mean of several analyses is given under I. After deducting a variable amount of carbonates (14.90 per cent. in the mean), the composition (II) of the angolite agrees with the formula $H_2Mn_3(SiO_3)_4 \cdot H_2O$. Angolite is a zeolite related to apophyllite or heulandite, and perhaps to inesite.

	SiO ₂ .	FeO.	MnO.	CaO.	MgO.	CO ₂ .	H ₂ O.	Total.
I.	41.89	1.23	35.79	7.51	0.90	6.49	6.30	100.11
II.	49.21	43.39		—	—	—	7.40	100.00

L. J. S.

Corundum-bearing Rocks of Eastern Ontario. By WILLET G. MILLER (*Amer. Geologist*, 1899, 24, 276—282).—Corundum occurs in Eastern Ontario in syenites, syenite-pegmatites, nephelite-syenites, and anorthosites, which as large masses are intrusive in the gneiss of the region; these occurrences are similar to those of India and the Urals (Abstr., 1899, ii, 763). A specimen of the anorthosite free from corundum from South Sherbrooke gave analysis I (by W. Lawson); the felspar (bytownite, Ab_1An_4) from the same rock gave II, and the hornblende gave III (in III also a trace of MnO).

	SiO ₂ .	Al ₂ O ₃ .	Fe ₂ O ₃ .	FeO.	CaO.	MgO.	Na ₂ O.	K ₂ O.	CO ₂ .	H ₂ O.	Total.	Sp. gr.
I.	47.32	30.36	1.35	1.55	15.45	2.44	1.88	0.66	0.58	0.10	101.69	2.73
II.	48.12	34.54	0.36	—	16.30	trace	1.91	0.15	—	nil	101.38	2.731
III.	41.40	15.39	7.01	7.17	12.53	10.31	3.58	1.56	—	0.81	99.76	3.18

L. J. S.

Meteorite from Oakley, Kansas. By H. L. PRESTON (*Amer. J. Sci.*, 1900, [iv], 9, 410—412).—This stone, which weighs 27.9 kilograms, was found 15 miles south-west of Oakley, Logan Co., Kansas, in 1895. The material is greyish-black with darker blotches and numerous grains of metallic iron and troilite. Under the microscope, it shows condrules of olivine and enstatite set in a very irregularly granular ground-mass of the same materials. Sp. gr. 3.7. The metallic portion (14.44 per cent. of the whole) contains Fe, 89.16; Ni, 10.84 per cent.

A list is given of eleven meteorites reported from Kansas, and it is suggested that five of these belong to the same fall. L. J. S.

Analyses of French Mineral Waters. By ADOLPHE CARNOT (*Ann. des Mines*, 1899, [ix], 16, 33—94).—A collection is given of 122 analyses of mineral waters from France and her colonies which

have been performed since 1894 in the Laboratory of the National School of Mines. Previous collections of 255 and 207 analyses were published in 1884 and 1894 respectively.

L. J. S.

Physiological Chemistry.

Digestion in Birds. By L. PAIRA-MALL (*Pflüger's Archiv*, 1900, 80, 600—627).—In pigeons and hens, during hunger, the gastric cells are laden with granules of ferment or zymogen. These granules are believed to be converted into the enzyme by the acid formed. The amount of pepsin obtainable from the mucous membrane continuously diminishes during digestion, reaching its minimum 6 to 8 hours after the meal. Restoration begins 2 or 3 hours later. The gizzard does not form pepsin. The gullet and crop secrete only mucus. The so-called middle-stomach of crows and magpies forms pepsin in the same way as described above. The histological changes in the cells of the pancreas are similar to those described by Heidenhain in the dog. This gland forms both proteolytic and amylolytic enzymes.

W. D. H.

Peptic Digestion. By EMIL SCHÜTZ and KARL H. HUPPERT (*Pflüger's Archiv*, 1900, 80, 470—526).—The experiments were conducted with egg-albumin freed from globulin; ovo-mucoid is not affected by gastric digestion, or may be removed by boiling with neutral ferric acetate. Determinations, mainly by the polarimeter, were made after digestion with artificial gastric juice of (1) acid-albumin, (2) primary proteoses, (3) secondary proteoses. The results are given in tables, and show the influence of temperature, of the degree of acidity, of the amount of albumin originally taken, of the length of time of digestion, of the volume of the fluid, and of the amount of pepsin on the relative quantities of the three groups of products just mentioned.

W. D. H.

The Bile as a Digestive Juice. By G. G. BRUNO (*Chem. Centr.*, 1900, i, 916; from *Arch. Sci. biol. St. Petersburg*, 7, 87—142).—The flow of bile ceases when the stomach is empty; it begins to flow with the entrance of food into the stomach. Water, proteid, or carbohydrate does not intensify the rate of secretion, but fat does.

The bile contains a proteolytic and a fat-splitting enzyme. It also assists the pancreatic juice in all its activities.

W. D. H.

Secretion of the Pancreas. By A. A. WALTER (*Chem. Centr.*, 1900, i, 916; from *Arch. Sci. biol. St. Petersburg*, 7, 1—86).—The secretion of pancreatic juice in dogs is stimulated by the hydrochloric acid of the stomach, and this largely depends on the appetite of the animal. The amount of secretion runs parallel with the amount of water in the food. Food rich in proteid, carbohydrate and fat calls forth respectively an increase of trypsin, amylpsin, and steapsin.

High acidity of the gastric is accompanied by high alkalinity of the pancreatic juice. The signal for all these reflex effects is the stimulation of the nerve-endings of the intestinal mucous membrane.

W. D. H.

Metabolism in Horses. By THEODOR PFEIFFER (*Landw. Versuchs-Stat.*, 1900, 54, 101—112. Compare *J. Landw.*, 1890, 38, 258).—A criticism of Zuntz and Lehmann's methods and conclusions (*Abstr.*, 1889, 911; *Landw. Versuchs-Stat.*, 1891, 38, 340; and *Landw. Jahrb.*, 1894, 23, 125, and 1898, 27, *Ergänzungsbd.*, iii). Respiration experiments during short periods furnish data as regards the direction of metabolism under different conditions, but cannot show exactly the absolute extent of the effects of the feeding.

N. H. J. M.

Influence of Extract of Ovaries on the Changes Produced in Nutrition During Pregnancy. By ALBERT CHARRIN and GUILLEMONAT (*Compt. rend.*, 1900, 130, 1787—1789).—During pregnancy, the activity of the organs of nutrition is notably diminished, less oxygen being consumed, and smaller quantities of carbon dioxide and urea eliminated. Injections of extracts of liver, spleen, and muscle do not stimulate these organs to any appreciable extent, whereas the extract of one or two ovaries, obtained by digesting these glands with a dilute solution of glycerol and sodium chloride, has a marked effect in increasing the excretion of urea. This result can only be maintained, however, by repeating the injection at least once in three days.

G. T. M.

Action of Increased Osmotic Pressure on the Ovum. By E. BATAILLON (*Compt. rend.*, 1900, 130, 1480—1482).—By placing the egg-cells of *Petromyzon* in isotonic solutions of salt or sugar, the separation of the blastosphere into its early segmentation spheres is accelerated, and may even result in a complete division, and formation of two embryos. Similar mechanical processes may possibly explain the occurrence of double monsters, or other abnormalities, in the higher animals.

W. D. H.

Relationship between the Nitrogen and Chlorides of the Stomach-contents. By JUSTIN WINTER and FALLOISE (*Compt. rend.*, 1900, 130, 1646—1648).—Attention is drawn to a fixed relationship which exists between the chlorine of the gastric juice and the amount of nitrogenous substances which pass into solution. This ratio is expressed by a mathematical formula.

W. D. H.

Thiocyanate in Human Saliva. By LAFAYETTE B. MENDEL and E. C. SCHNEIDER (*Proc. Amer. Physiol. Soc.*, 1900, vii—viii; *Amer. J. Physiol.*, 4).—The saliva of non-smokers and smokers shows an average of 0.0029 and 0.0134 of potassium thiocyanate per cent. respectively. The parotid saliva is uniformly richer in this substance than the submaxillary saliva.

W. D. H.

Action of Anti-leucocytic Serums on Blood-coagulation. By C. DELEZENNE (*Compt. rend.*, 1900, 130, 1488—1490. Compare this vol., ii, 423).—Further experiments are brought forward to show that certain serums like 'peptone' when injected intra-

venously lead to the liberation of an anti-coagulating substance. The importance of the liver as well as of the leucocytes is insisted on. Probably, when the leucocytes disintegrate, two substances are liberated, one assisting, the other hindering, coagulation of the blood; the former is retained by the liver, the latter remains in the blood.

W. D. H.

Iodine in the Blood. By EUGÈNE GLEY and PAUL BOURCET (*Compt. rend.*, 1900, 130, 1721—1724).—In the blood of the dog, iodine combined with nucleo-proteid is present normally in solution. Its amount, like that of iodine in the thyroid, is variable. In the analyses quoted, the amount of iodine in the thyroid varied from 0.18 to 1.06, and in a litre of blood from 0.013 to 0.11 milligram.

W. D. H.

Artificial Production of Normal Larvæ from Unfertilised Eggs of the Sea Urchin. By JACQUES LOEB (*Amer. J. Physiol.*, 1900, 3, 434—471).—The paper describes in full a large number of experiments which show that the eggs of the sea urchin will develop with somewhat imperfect embryos even though fertilisation has not occurred. To promote this, 'physiologically balanced salt solutions' were used similar to those employed previously in the study of muscular contraction and other vital contractile phenomena.

W. D. H.

Organic Substance of the Shells of *Mytilus* and *Pinna*. By G. WETZEL (*Zeit. physiol. Chem.*, 1900, 29, 386—410).—The organic basis of the shells of *Mytilus* and *Pinna* is mainly conchiolin. On being decomposed by sulphuric acid, it yields tyrosine, leucine, and glycine. The occurrence of phenylaminopropionic acid or other phenyl-amino-acids is not probable. It contains also a 'hexon' nucleus; the yield of bases places it between casein and egg-albumin. The quantity of nitrogen split off as ammonia amounts to 3.47 per cent. of the whole. The organic residue of the mother-of-pearl substance of the mussel shell differs from that obtained from the rest of the shell by a smaller percentage of carbon.

W. D. H.

Mucin. By ISAAC LEVIN (*Amer. J. Physiol.*, 1900, 4, 90—95).—Mucin prepared from connective tissue, when injected into the blood-stream of dogs and rabbits, produces a depressive effect on the central nervous system, which is chiefly shown by a fall of blood-pressure. It is, however, not fatal unless the animal has been previously deprived of its thyroid. Mucinæmia may be one of the pathological conditions resulting from the absence of the thyroid function.

W. D. H.

Chemistry of Paranucleo-compounds. By P. A. LEVENE and C. L. ALSBERG (*Proc. Amer. Physiol. Soc.*, 1900, xi; *Amer. J. Physiol.*, 4).—The ichthulin of the cod-fish egg differs from that described by Walter in its percentage composition and in containing no carbohydrate radicle in its molecule. On treatment with alkalis, both ovotellin and ichthulin yield substances akin to true nucleic acids, but differing from them in the absence of purine bases, and in containing proteid in their molecule. This proteid does not resemble the protamines, as can be concluded by the yield of 'hexon' bases. Iron

enters into the molecule of the paranucleins in a combination probably similar to that of the ethereal acids. W. D. H.

Chemistry of the Lymphatic Glands. By LAFAYETTE B. MENDEL and R. NAKASEKO (*Proc. Amer. Physiol. Soc.*, 1900, xii; *Amer. J. Physiol.*, 4).—In view of a possible compensatory action of the lymphatic glands after splenectomy (an operation which does not lessen uric acid excretion), the Horbaczewski-Spitzer experiments were repeated with these organs. At most, only traces of uric acid were obtained by treatment of 100–300 grams of material. Xanthine bases were found in larger quantity. The glands are rich in nucleic acid, the study of which is being continued. W. D. H.

Urea in Human Milk. By BERNHARD SCHÖNDORFF (*Pflüger's Archiv*, 1900, 81, 42–47).—Polemical. The values for urea in human milk given previously are maintained to be correct, and those given by Camerer and Söldner incorrect, and much too small. W. D. H.

Xanthine Bases in Fæces. By WILLIAM H. PARKER (*Amer. J. Physiol.*, 1900, 4, 83–89).—From experiments on man, it is found that under normal conditions on a diet containing no nuclein there is a constant excretion of combined xanthine bases derived from the cells of the alimentary canal. The amount excreted is about 30 milligrams a day, and is about equal to that which leaves the body by the urine under the same conditions. The amount is nearly doubled with a mixed diet. This increase may not be necessarily due to the nuclein and alloxuric substances in the food, but may arise indirectly from an influence exerted on the processes of metabolism and secretion. W. D. H.

Excretion of Sulphur after Extirpation of the Liver. By S. LANG (*Zeit. physiol. Chem.*, 1900, 29, 305–319).—After the extirpation of the liver in birds, the amount and relationships of the various forms of sulphur in the urine show no noteworthy departure from the normal. The liver plays practically no part in the formation of sulphuric acid from the sulphur of the food. W. D. H.

Albumin in Normal Urine. By A. BELLOCQ (*J. Pharm.*, 1900, [vi], 11, 478–482).—After carefully defining what shall be considered as “normal” urine, the author states that the latter produces a faint turbidity with Tanret's iodo-mercuric reagent in presence of a saturated solution of citric acid. This turbidity, although almost unnoticeable alone, is distinctly visible when compared with the original limpid urine. Finely-divided manganese dioxide carries down from normal urine the whole of its albumin, the latter being recovered as a whitish mucilage; on dissolving the dioxide in a saturated solution of sulphurous acid, adding 30 per cent. of alcohol of 85° containing citric acid, and filtering, ordinary albumin contaminated with uric acid is obtained. W. A. D.

Decrease of Water in the Central Nervous System of the Growing White Rat. By HENRY H. DONALDSON (*Proc. Amer. Physiol. Soc.*, 1900, v—vi; *Amer. J. Physiol.*, 4).—In the spinal cord of rats,

the percentage of water decreases from 85 at birth to 70 in old age; in the brain the numbers respectively are 88 and 77.5. The most rapid stage of loss of water is from the tenth to the fiftieth day of life, the period during which the process of myelination of the nerve fibres is proceeding most rapidly. W. D. H.

Physiological Action of Extracts of Sympathetic Ganglia. By ALLEN CLEGHORN (*J. Boston Soc. Med. Sciences*, 1900, 4, 239—242. Compare Abstr., 1899, ii, 569, and this vol., ii, 423).—The idea that choline is the substance responsible for the fall of blood-pressure produced by the injection of extracts of sympathetic ganglia is combated. The extracts in the present experiments were made with alcohol; this was evaporated off, and the residue dissolved in saline solution. Choline is admittedly present, but after the removal of choline by platinic chloride and filtering, the filtrate was evaporated to dryness, and the residue extracted with saline solution. Injection of this still produced a fall of blood-pressure. Moreover, it is stated that the depressor effect of the ganglionic extract is not abolished by atropine. W. D. H.

The Anti-rennin of Serum in Pathological Conditions. By CH. ACHARD and A. CLERC (*Compt. rend.*, 1900, 130, 1727—1729).—Previous observers have shown that normal blood-serum contains some substance which hinders the action of rennin on milk. In the present research, thirty-four human serums from various cases of disease were examined, with the general result that the anti-rennin substance diminishes in grave pathological disorders. W. D. H.

Analysis of the Liquid contained in a Mesenteric Cyst. By A. RICHAUD and R. BONNEAU (*J. Pharm.*, 1900, [vi], 11, 535—541).—The liquid had a sp. gr. 1.025, an alkaline reaction, and did not deposit fibrin after 18 hours; it contained 94.14 per cent. of water, 4.15 per cent. of proteid material (precipitated by alcohol acidified with acetic acid), 0.45 per cent. of fat, 0.77 per cent. of extractives, and gave a solid residue of 5.86 per cent., and 0.49 per cent. of ash. The ash contained sulphates, chlorides, and carbonates, but no phosphates. On adding an excess of alcohol of 95°, a viscous, fibrous mass of proteids was precipitated; this mass shared the character of both the true and the pseudo-mucins, since on heating with dilute sulphuric acid for 1 hour at 115—120° it yielded a substance having reducing properties (reaction of true mucin), and yet on peptic digestion gave an ash rich in phosphorus (characteristic of pseudo-mucin). Finally, it is noteworthy that the secretion contained only minute quantities of serin, globulin, or casein. W. A. D.

Action of Diphtheria Toxin on the Motor Cells of the Spinal Cord. By H. RAINY (*J. Pathol. and Bacteriol.*, 1900, 6, 435—458).—Diphtheritic paralysis is associated, not only with changes in peripheral nerves, but also with alterations in the cord itself, namely, moderate chromatolysis and vacuolation of the protoplasm of the motor cells. W. D. H.

Diphtheritic Paralysis and Antitoxin. By F. RANSOM (*J. Pathol. and Bacteriol.*, 1900, 6, 397—414).—Experiments on animals

show that with suitable doses, the administration of antitoxin prevents the development of paralysis caused by the diphtheritic toxin.

W. D. H.

The Lymph after Intravenous Injection of Tetanus Toxin and Antitoxin. By F. RANSOM (*Zeit. physiol. Chem.*, 1900, 29, 349—372).—After the injection of the tetanus poison into the bloodstream, an important part of it passes rapidly into the lymph, and after 26 hours, the amounts in blood and lymph are about equal. If the thoracic duct is opened before the injection of the toxin, so that the lymph drains away, the toxic value of the blood remains, for at least 6 hours, higher than that of the lymph. Much the same is true for the antitoxic horse-serum, except that even 68 hours after the injection the blood still contains more antitoxin than the lymph. The toxin thus behaves like an inorganic constituent, and the antitoxin like a proteid constituent of the blood-lymph system.

W. D. H.

Interaction of Toxin and Antitoxin. By WALTER MYERS (*J. Pathol. and Bacteriol.*, 1900, 6, 415—434).—In cobra venom there are two poisons, one, *cobralysin*, acts hæmolytically, the other, *cobraneurin*, causes death by its action on the respiratory centre. The present paper relates principally to the first, and to the methods by means of which it may be estimated physiologically, and the amount of anti-venene necessary to neutralise it. Ehrlich's methods appear to have guided the experiments, and the formation of toxoids is confirmed. This combines with antitoxin, but does not act on the blood corpuscles.

W. D. H.

Use of Alkaline Solutions in Surgical Shock. By WILLIAM H. HOWELL (*Proc. Amer. Physiol. Soc.*, 1900, xiv—xv; *Amer. J. Physiol.*, 4).—Conditions of shock in animals produced, for instance, by operations on the brain, are associated with heart failure and fall of blood pressure. This can be largely counteracted by the injection of 0.5 per cent. solution of sodium carbonate into the veins or into the rectum. If injection is made into the veins, care must be taken to use a moderate amount of solution, not more than sufficient to raise the alkalinity of the blood by 0.1 to 0.2 per cent. Rectal injections are safer. 'Shock-blood' contains no poisonous substances.

W. D. H.

Action of Phloridzin on Muscle. By FREDERIC S. LEE and C. C. HARROLD (*Proc. Amer. Physiol. Soc.*, 1900, ix—x; *Amer. J. Physiol.*, 4).—One gram of phloridzin was injected three times daily for two to four days into fasting cats. The course of fatigue in the *tibialis anticus* muscle was then studied, when the animals were killed. Instead of giving 800 to 1000 contractions, it gives only 200 to 400, and the curves obtained resemble those obtained in the last stages of normal fatigue. This is due to removal of carbohydrates; subsequent injection of dextrose largely restores the muscle. Phloridzinised muscle rapidly goes into rigor.

W. D. H.

Influence of Phloridzin Diabetes on Lactation. By GRAHAM LUSK (*Proc. Amer. Physiol. Soc.*, 1900, xi; *Amer. J. Physiol.*, 4).—In fasting goats, phloridzin diabetes stops milk formation. This is

probably the result of the diabetes, and not of the specific action of phloridzin on the gland. In sugar elimination, the fasting goat resembles the rabbit, since in the urine the ratio of dextrose to nitrogen is 2.8 to 1.

W. D. H.

Toxicity of Urine. By ALBERT CHARRIN (*Compt. rend.*, 1900, 130, 1724—1726).—Support is given to Bouchard's views of auto-intoxication, and that the toxicity of urine is, at any rate in part, due to products of katabolism.

W. D. H.

Action on the Heart of Toxic Products of the Typhoid Bacillus. By GEORGE T. KEMP and MISS S. L. DEWEY (*Proc. Amer. Physiol. Soc.*, 1900, viii—ix; *Amer. J. Physiol.*, 4).—The culture medium used was alkali-albumin prepared from egg white plus Ringer's solution in the proportion 1 : 10. This has no action on the heart. The cultures of the typhoid bacillus were filtered, and tested on terrapins' hearts. The heart is gradually weakened without being slowed, and it finally stops in diastole. If the poison has not acted too long, the heart can be revived by Ringer's solution. This property is associated with the presence of proteid (albumin or globulin); the alcoholic filtrate, which is proteid-free, when evaporated to dryness and dissolved in Ringer's solution, increases the strength of the heart-beat without affecting the rate; the proteid precipitate, dissolved in the same solution, gives the same effect on the heart as the culture, but is somewhat less powerful.

W. D. H.

Combination of Nucleins with Metallic Compounds, Alkaloids, and Toxins. By H. STASSANO (*Compt. rend.*, 1900, 131, 72—74).—Ammonium hydrosulphide has no immediate action on mercury and arsenic contained in the nuclein derived from animals poisoned with compounds of these metals. The mercury may be eliminated by electrolysis, but less rapidly than from solutions of its salts, and the separation is accompanied by the destruction of the nuclein by the electric current. An aqueous solution of hæmatoxylin, which is rendered turbid by mercuric chloride dissolved in water or serum, remains unaltered in nuclein solutions containing mercury. These results indicate that the metallic radicles are actually in combination with the nuclein.

Morphine and strychnine can be rapidly extracted by ether from alkaline mixtures of the nucleins; the alkaloids are also liberated by electrolysis, the action being attended by the decomposition of the nuclein. The separation of nucleins from animal tissues by peptic digestion requires two days, whereas the nucleo-albumins can be isolated in one hour; the alkaloids may be eliminated from the latter substances quite as readily as from the former.

The nucleo-albumins prepared from the liver, spleen, and kidneys of dogs poisoned with ricin or tetanin are subjected to the action of a feeble electric current until the decomposition of the nuclein compounds is complete. The toxin and proteids are then precipitated together by alcohol, and from the precipitate the base is extracted with brine.

G. T. M.

Chemistry of Vegetable Physiology and Agriculture.

Mechanism of Agglutination. By HAROLD C. ERNST and W. H. ROBEY, jun. (*J. Boston Soc. Med. Sciences*, 1900, 4, 219—228).—A discussion with experimental tests of the numerous theories put forward to explain agglutination. No satisfactory theory to account for all cases has yet been offered, although Bordet's, that an agglutinating agent (agglutinine) acting upon an agglutinable substance of at present uncertain nature, is regarded as most rational. The reaction occurs, not only with bacteria, but with many other elements, globules, casein, and various precipitates.
W. D. H.

Antiseptic Value of Certain Chemicals in Milk. By S. MOULTON BABCOCK, H. L. RUSSELL, and ALFRED VIVIAN (*15th Ann. Rep. Agr. Expt. Stat. Univ. Wisconsin*, 1898, 98—103).—For the purpose of experiments on the enzymes of milk, it was desired to obtain an antiseptic which would act on the organised ferments without materially affecting the enzymes. Benzene, chloroform, ether, toluene, xylene, aniline, arsenious acid, thymene, phenol, sodium fluoride, oil of cloves, oil of cassia, oil of Ceylon cinnamon, oil of mustard, and turpentine were the substances tried.

It was found that the antiseptic efficiency of many substances is much less in milk than in liquids which do not contain substances like fat, which combines with the antiseptic and thus diminishes its power. Only four, chloroform, ether, benzene, and toluene, are to be recommended in studying the enzymes, and a distinction has to be made between curdling and the proteolytic action; ether retards curdling, whilst scarcely any difference exists in the time of curdling with the other three substances. Chloroform and ether seem to affect the digestive changes least. Chloroform is the best agent, and 2—3 per cent. keeps milk perfectly. Owing to its high sp. gr. and its affinity for fat, the cream is submerged, and this renders sampling more accurate.
N. H. J. M.

Boric Acid and Formaldehyde as Milk Preservatives. By SAMUEL RIDEAL and A. G. R. FOULERTON (*Exper. Stat. Record*, 1900, 11, 582; from *Public Health*, 1899, 11, 554—568).—The minimum amounts of the substances to preserve milk for 24 hours were found to be 1 in 50,000 for formaldehyde, and 0.05 per cent. of a mixture of boric acid and borax. These amounts have no appreciable effect on the proteolytic action of the peptic and pancreatic enzymes. The boric acid mixture distinctly retarded the amylolytic action of saliva, but it is doubtful if this is of importance; the action of formaldehyde was much less marked.

The results of experiments with kittens, a rabbit, and guinea-pigs indicated that the amount of formaldehyde required to preserve milk has no marked effect on proteid metabolism. Fishes were not appreciably affected by being kept for 6 days in water containing 1 part of

formaldehyde in 50,000, and a less dilute solution (1:20,000) did not seem to affect frogs in 2 hours.

The conclusions are drawn that the two substances, in the quantities as given, are effective preservatives for milk for 24 hours, and that they have no appreciable effect on the digestibility of the milk.

N. H. J. M.

Boric Acid and Formaldehyde as Food Preservatives. By OTTO HEHNER (*Exper. Stat. Record*, 1900, 11, 582—583; from *Brit. Food Jour.*, 1899, 1, 132).—The experiments of Rideal and Foulerton (preceding abstract) are criticised, on the ground that there were no control animals. The author is inclined to infer from the results that the preservatives, in the amounts recommended, are injurious.

N. H. J. M.

Action of Dry and Moist Air on Plants. By EBERHARDT (*Compt. rend.*, 1900, 131, 193—196).—Germinating plants develop more rapidly in air saturated with moisture than in dry or normal air; the stem is longer, but has a smaller diameter; the number of leaves is greater, but the production of rootlets is greatly diminished. Dry air decreases the development of the stem and leaves, the former, however, having a greater diameter than that of the plant grown under normal conditions; the foliage surface is diminished, whilst the number of rootlets is increased.

G. T. M.

Can Strontium and Barium replace Calcium in Phænogams? By U. SUZUKI (*Bul. Coll. Agr. Tokyo Imp. Univ.*, 1900, 4, 69—79).—Sand culture experiments with buckwheat and barley, and water culture experiments with *Phlox paniculata*, *Rubus Idæus*, and *Coreopsis tinctoria* are described. It was found that neither strontium nor barium can replace calcium, and that their salts are both strongly poisonous. Haselhoff's statement that strontium can replace calcium (Abstr., 1894, ii, 207) is therefore incorrect.

The poisonous effects of barium and strontium are diminished by the presence of calcium.*

The author considers that Loew's view as to the rôle of calcium (Abstr., 1899, ii, 789) agrees best with his observations.

N. H. J. M.

Distribution of Cane Sugar in Plants. By JUSTUS ANDERSEN (*Zeit. physiol. Chem.*, 1900, 29, 423—428).—The wide distribution of cane sugar in the vegetable world has been pointed out by Schulze. His investigations relate chiefly to the higher plants. The cryptogams still require to be investigated, and in the present paper it is shown that cane sugar is present in a number of ferns.

W. D. H.

Reserve Carbohydrate of the Seed of *Trifolium Repens*. By HENRI HÉRISSEY (*Compt. rend.*, 1900, 130, 1719—1721. Compare Abstr., 1899, i, 839, and this vol., ii, 233).—The carbohydrate obtained from the seeds of *Trifolium repens* by extraction with cold water con-

* Haselhoff (Abstr., 1896, ii, 267) found that very small amounts of barium are injurious, and suggested that addition of lime would lessen its effects.

taining lead acetate and precipitation of the filtered solution with alcohol, is a *mannogalactan*, for on hydrolysis with dilute sulphuric acid or seminase it yields galactose and mannose; a 1 per cent. solution gives $[\alpha]_D 81.1^\circ$.
G. T. M.

Composition of the Albumen of the Seed of the American Bean (*Gleditschia triacanthos*). By MAURICE GORET (*Compt. rend.*, 1900, 131, 60—63).—The albumen of the seed of the American bean (*Gleditschia triacanthos*) when hydrolysed at 110° with excess of 2 per cent. sulphuric acid yields 94.20 per cent. of reducing sugar; the soluble ferment seminase obtained from lucerne (Bourquelot and Hérissé, this vol., ii, 135, 233) has a similar hydrolytic action.

The reducing sugar contains about 70 per cent. of galactose and 23 per cent. of mannose; both constituents were isolated in a crystalline form, the former being estimated as mucic acid and the latter as mannose hydrazone.

It follows that this albumen is either a mannogalactan or a mixture of mannan and galactan (compare Abstr., 1899, i, 868, and ii, 301, 917).
G. T. M.

Arginine. By U. SUZUKI (*Bul. Coll. Agr. Tokyo Imp. Univ.*, 1900, 4, 1—24. Compare Schulze and Steiger, Abstr., 1886, 725; Schulze and Likiernik, *ibid.*, 1891, 1521; Hedin, *ibid.*, 1895, i, 160, and 1896, i, 193; Kossel, *ibid.*, 1896, i, 582; and 1898, i, 715; Schulze, *ibid.*, ii, 383 and 572; and 1898, ii, 179; Kutscher, *ibid.*, 1898, i, 161; Ellinger, *Ber.*, 31, 3183; and Gulewitsch, *Zeit. physiol. Chem.*, 27, 178).—The proteids obtained from the seeds of *Cryptomeria japonica*, *Pinus Thunbergii*, and *Gingko biloba* yielded much organic bases, chiefly arginine, when boiled with 20 per cent. hydrogen chloride (sp. gr. 1.10). The etiolated shoots of *Cryptomeria* and *Pinus* also contain much organic bases, chiefly arginine, but the shoots of *Gingko* yielded very little. It is probable that the chemical nature of the proteids of the shoots of coniferous plants is the same as that of the seed proteids, since both proteids furnish the same products of decomposition.

The method employed for the isolation of arginine is described.

N. H. J. M.

Formation of Arginine in Coniferous Plants. By U. SUZUKI (*Bul. Coll. Agr. Tokyo Imp. Univ.*, 1900, 4, 25—68. Compare E. Schulze, *Zeit. physiol. Chem.*, 22, 445).—The results of experiments with coniferous plants (*Pinus Thunbergii* and *Cryptomeria japonica*) showed that the arginine they contain is not only formed from the decomposition of proteids, but can be produced synthetically from ammonium salts and nitrates. This synthetical production of arginine takes place both in full and in diffused daylight, but it is not yet proved whether it proceeds in darkness.

There is a great accumulation of arginine in the shoots of coniferous plants in the dark, as well as in full daylight during the first stage of germination; it soon diminishes on further exposure to light, and gradually increases if the light is cut off. The transformation of arginine into proteids in presence of light is accelerated by the presence of mineral matter.

It is probable that arginine is directly used in regenerating proteids, but its relation to other amino-compounds requires further investigation. It seems, however, probable that there is a production of arginine from other amides.

From the results of experiments with *Brassica napa* and barley, the conclusion is drawn that in the case of plants other than coniferous, arginine is not formed from ammonium salts, asparagine being the only product.

N. H. J. M.

Amount of Alkaloids in the Bark of Java Pomegranates. By HEINRICH BECKURTS (*Arch. Pharm.*, 1900, 238, 8—9. Compare Ewers, *Abstr.*, 1899, ii, 457).—The percentage of alkaloids in bark from Java is found to be 0·92—0·98, that is, not much more than in the bark of roots from the South of France. In the titration of these alkaloids, iodeosin is to be preferred to methyl-orange as the indicator.

C. F. B.

[Composition of the Flowers of the] Hollyhock. By C. ZAY (*Landw. Versuchs-Stat.*, 1900, 54, 141—145).—The flowers of the hollyhock have the following percentage composition: Water, 13·15; crude fat, 2·29; crude fibre, 14·33; proteids, 6·56; nitrogenous matter other than proteids, 4·68; non-nitrogenous substances, 49·71; and ash, 9·28.

The flowers contain 0·67 per cent. of reducing sugar. The ethereal extract of the flowers yield a compound melting at 63·5—64°. It forms lustrous plates readily soluble in ether, petroleum, chloroform, or warm alcohol, and is not reddened by sulphuric acid.

N. H. J. M.

Composition of the Spores of *Aspergillus Oryzae*. By K. ASO (*Bul. Coll. Agr. Tokyo Imp. Univ.*, 1900, 4, 81—96).—The air-dried spores contained 57·485 per cent. of dry matter of the following percentage composition:

N.	Ether extract.	Alcohol extract.	Carbohydrates (as dextrose).	Crude fibre.	Ash.
6·380	0·377	27·666	20·017	8·994	5·151

Lecithin was detected in the ether extract, and the alcoholic extract which was obtained after extracting with ether was found to contain mannitol and trehalose.

The composition of the ash was found to be as follows:

K ₂ O.	Na ₂ O.	CaO.	MgO.	Fe ₂ O ₃ .	P ₂ O ₅ .	SO ₃ .	SiO ₂ .	Cl.
45·96	4·13	1·04	4·36	4·92	39·64	2·00	0·41	trace

N. H. J. M.

Metabolism in Full-grown Bullocks with Maintenance and Fattening Foods. By OSCAR KELLNER and A. KÖHLER (*Landw. Versuchs-Stat.*, 1900, 53, 1—16 and 398—474. Compare *Abstr.*, 1894, ii, 391, and *Landw. Versuchs-Stat.*, 1896, 47, 291 and 309).—In the experiments now described (see following abstracts), the effect of feeding with isolated foods, such as starch-meal, gluten-meal, oil, and cellulose, and of whole foods, as hay, cereal straw, and molasses, was determined by deducting the amounts of meat and fat produced

with a basal ration from the amounts obtained when the basal ration was employed in conjunction with the different foods.

Instead of adopting the usual method of calculating the results on 1000 lb. of live weight, the surface (compare Meek, *Zeits. Biol.*, 1879, 15, 425) of the beasts was taken into account, as it is on this that the losses of heat depend.

Among the factors which have to be taken into account in the experiments is the amount of water consumed. The raising of the temperature of the water to that of the body, and its elimination, cannot fail to be without influence. The amount of water consumed depends partly on the food; gluten-meal, molasses, hay, and straw increased, whilst starch-meal and oil diminished the consumption of water per kilogram of dry food.

As regards the production of hydrocarbons, 4.2 parts of methane were produced on the average from 100 parts of digested carbohydrate. Digestible protein and oil have no direct share in producing hydrocarbons; large amounts of oil hinder the production of hydrocarbons. The greatest quantity of hydrocarbon was obtained when wheat straw was employed. This is due, not only to the chemical composition of the straw, but to its physical nature and the fact that its digestion is slow.

Direct determinations of the heat of combustion of urine showed that, within certain limits of proteid-feeding, the amount of carbon in the urine is an approximately accurate measure of the heat value of the total dry matter of the urine, 1 gram of urine-carbon corresponding with about 10 Cal. With large amounts of gluten-meal, however, the carbon of the urine seems to be in compounds which yield more heat than was the case when the basal rations were employed alone. On the other hand, when the bullocks were fed with molasses, 1 gram of urine-carbon corresponded with less than 10 Cal., owing to the greater amounts of carbonates present.

By deducting the losses in urine and methane from the heat-value of 1 gram of digested organic matter, values are obtained indicating the amounts of heat produced by the decomposition of the digested substance in the organism, and also the relations in which the substances examined can replace each other in the maintenance food for bullocks. When starch is represented by 100, the following numbers show the isodynamic equivalents for the various foods: Earth-nut oil, 43; gluten protein, 76; extracted straw, 103; molasses, 103; hay, 103; oat straw, 100; and wheat straw, 113.

Owing to still greater losses than those due to formation of urine and methane, the values of the foods in producing flesh and fat are in every case below the "physiological values"—the heat value *minus* losses in urine and methane. The digestible organic matters of gluten-protein, starch, and molasses behave similarly, but the productive value of oil is decidedly higher, whilst in the case of hay and straw the values are lower than in the isolated components. The productive value of a substance depends therefore, not only on the amount of digestible matter it contains, but to an important extent on the nature of the tissues and on the amount of indigestible matter present.

Calculations of the amounts of digestible organic matter required to produce the same amounts of flesh and fat, over the minimum amounts required by the beasts, gave the following results: Starch meal, 100; gluten meal, 99; earth-nut oil, 45; extracted straw, 96; molasses, 97; hay, 147; oat straw, 157; and wheat straw, 374.

With full-grown bullocks, fattening rations with wide nutritive ratios can produce the same results as rations richer in proteids.

N. H. J. M.

Experiments with Gluten and Starch Meal. By OSCAR KELLNER, A. KÖHLER, F. BARNSTEIN, W. ZIELSTORFF, H. LÜHRIG, and F. MACH (*Landw. Versuchs-Stat.*, 1900, 53, 17—95).—In these experiments, which extended over some months, the amounts of food and water consumed, the changes in live weight, the amount and composition of the fæces and urine, and the amounts of carbon dioxide and hydrocarbon produced were determined; daily observations of the temperature of the stalls were also made.

When the amount of starch was increased so as to give a nutritive ratio of 1:15·95 or 1:16·21, considerable amounts of starch passed into the fæces, and the digestion of crude fibre was diminished.

Three concordant results showed that 86 per cent. of the crude proteid of gluten meal is digested.

In all the experiments, there was considerable production of hydrocarbon.

The production of fat by no means depends on proteid-feeding. Nitrogenous food produces for some time a greater increase of flesh than food poor in nitrogen, but the production of meat is not in proportion to the amount of digestible nitrogen in the food. Taking the average of both experiments, 1 kilogram of total food produced 219·7, 217·1, and 224·2 grams of flesh and fat when the nutritive ratios were 1:4, 1:10—11, and 1:16 respectively. The average amounts of increase produced by 1 kilogram of digestible food available for production by addition of gluten and starch were with (1) gluten meal, 229·7, and (2) starch meal, 250·6 grams.

The utilisation of the available energy of starch meal was on the whole higher than was the case with proteid.

N. H. J. M.

Experiments with Gluten, Starch Meal, and Oil. By OSCAR KELLNER, A. KÖHLER, W. ZIELSTORFF, FR. HERING, R. EWERT, and M. LEHMANN (*Landw. Versuchs-Stat.*, 1900, 53, 96—171).—During the first period of the experiments, the bullocks were fed with limited fattening food; in the second period, starch meal was given; in the third period, an amount of oil approximately isodynamic with the starch; and in the fourth period gluten meal.

The amount of carbon dioxide contained in the water consumed was determined.

The increase produced by 1 kilogram of the different foods was as follows: Starch meal, 215·8; earth-nut oil (reckoned as starch), 203·7; and gluten meal, 170·9 grams. As one part of oil is calculated to 2·27 parts of starch, the increase due to 1 kilogram of oil would be 462·4 grams.

N. H. J. M.

Experiments with Meadow Hay, Oat Straw, Starch Meal, and Molasses. By OSCAR KELLNER, A. KÖHLER, M. LEHMANN, FR. HERING, K. WEDEMEYER, and TH. METHNER (*Landw. Versuchs-Stat.*, 1900, 53, 172—277).—The results of experiments with two bullocks gave the following average amounts of increase for 1 kilogram of the food: Meadow hay, 149·7; oat straw, 148·7; starch meal, 255·8; earth-nut oil, 416·1; and molasses, 258·0 grams.

With exception of hay and oat straw, the numbers are not exact, and are, especially in the case of oil, too high.

Taking into account the alteration in live weight and surface, calculations are given of the percentage amounts of available energy in the increase. The results show that earth-nut oil takes the first place, (65·2—70·6 per cent.), then starch meal (65·2—66·0 per cent.) and molasses (60·3 per cent.). Meadow hay and oat straw gave much lower results (42·8—37·7 and 39·9—35·2 per cent.).

Hay, oat straw, and starch produced the greatest amounts of methane; oil, in some cases, diminished the amount of hydrocarbon produced from the other foods.

N. H. J. M.

Experiments with Meadow Hay, Wheat Straw, Starch Meal, Extracted Rye Straw, and Molasses. By OSCAR KELLNER, A. KÖHLER, M. LEHMANN, FR. HERING, K. WEDEMEYER, J. VOLHARD, H. PETERS, H. VON GILLERN, and O. ZAHN (*Landw. Versuchs-Stat.*, 1900, 53, 278—397).—The extracted rye straw was prepared by heating the straw (1 kilo.) under pressure with a solution (2070 c.c.) containing NaOH, 55; Na_2CO_3 , 20; and $\text{Na}_2\text{S} + \text{Na}_2\text{S}_2\text{O}_3$, 22 grams per litre.

It was found that the cellulose of the extracted straw was of not less effect than starch, whilst the digestible matter of wheat straw, oat straw, and meadow hay produce much less increase. This difference is attributed to the presence, in the raw foods, of lignin-like substances. The raw foods require a greater expenditure of energy in chewing and digesting, and the passage of sparingly soluble matter into the lower intestines results in a loss of substance otherwise available for production of increase.

N. H. J. M.

Beet Molasses of Different Origin. By OSCAR KELLNER, H. PETERS, O. ZAHN, and A. STRIGEL (*Landw. Versuchs-Stat.*, 1900, 54, 113—123).—The molasses was in each case obtained from factories in which the diffusion process was employed. Molasses obtained directly from the juice contained more ash, nitrogen, and organic non-sugar than when the strontium process is used. The cane-sugar in the dry matter is about the same in both cases, but the dry matter of molasses from the strontium process contained 15·1 per cent. of raffinose.

The sp. gr. of the dry matter differed only slightly (1·679—1·709), and the results gave an average (1·692) almost identical with the number (1·69) obtained by Neubauer (*Landw. Versuchs-Stat.*, 1899, 51, 421).

N. H. J. M.

Milk and Artificial Foods for Fattening Calves. By D. DICKSON and L. MALPEAUX (*Ann. Agron.*, 1900, 26, 217—245).—Feeding with milk gives the best results both as regards amount and

quality. As regards substitutes for milk, starch and malt flour proved to be the best of the foods employed; but even with these it is an advantage to terminate the fattening with milk.

Decoction of linseed in conjunction with rice starch or flour gave good results as regards quality, whilst boiled malt flour mixed with skim milk also gives very good results. Margarine and sugar may be employed with milk from which the cream has been partially separated, and it is suggested that to separate the cream and replace it by margarine for calves is preferable to employing margarine for human consumption.

Many foods remain to be tried, and it is possible that some may furnish better results than those employed in the experiments described.

N. H. J. M.

Effect of Fatigue on the Quantity and Quality of Milk.

By JOSEF L. HILLS (*12th Ann. Rep. Vermont Agr. Expt. Stat.*, 1898—1899, 309).—The cows had been driven about 10 miles, sent 70 miles by rail, the whole journey taking about 18 hours, during which time they were not milked. The amount (in lbs.) and percentage composition of the milk the day after arriving, and after 1 and 3 weeks, was as follows:

Amount (lbs.).			Total solids.			Fat.			Solids, not fat.		
1.	2.	3.	1.	2.	3.	1.	2.	3.	1.	2.	3.
122.5	122.3	131.4	15.19	13.73	14.10	5.94	4.43	4.82	9.25	9.30	9.28

The results show that milk should not be tested until the cows have recovered from the effects of fatigue.

N. H. J. M.

Effect of Food on the Hardness of Butter, and Composition of Butter Fat. By JAMES M. BARTLET (*14th Ann. Rept. Maine Agr. Expt. Stat.* for 1898, 97—113).—The object of the experiments was to ascertain the effect of different gluten meals on butter. Three kinds of meals were employed containing respectively about 15, 8, and less than 3 per cent. of fat. In one experiment with the meal containing the lowest percentage of oil, emulsified tallow was added to the food.

The results show that the hardness of butter can, to a great extent, be regulated by the food. Gluten products containing much oil produce soft butter; gluten meals with 3 per cent. of fat or less, and with high percentages of proteids, will make butter sufficiently hard when employed in conjunction with maize meal and bran. When freed from fat, the gluteins will not, however, have the hardening effect of cotton seed meal.

The melting point of fat, as determined by the American official method, is not a true indication of the hardness; some fats of medium hard butters gave melting points practically the same as the softest butters. When, however, the melting point of the fat is low and the iodine number high, the butter is soft, and *vice versa*.

The production of soft butter cannot be attributed either to deficiency of nitrogenous food or to excess of fat; addition of 0.5 lb. of tallow to the ration caused the butter to become harder, and raised the melting point of the butter-fat. In some way, the properties of the food-fat are transmitted to the milk-fat.

N. H. J. M.

Effect of Feeding Fat on the Percentage of Fat in the Milk.

By JAMES M. BARTLET (14th Ann. Rep. Maine Agr. Expt. Stat. for 1898, 114—117).—Albert and Maercker (*Landw. Jahrb.*, 1898, 27) found that rations rich in fat caused a decided increase in the fat of the milk; in another experiment it was found that in a longer period the yield of fat afterwards fell to about the same as it was previously with a ration poor in fat. The falling off was attributed to over-feeding with fat. Rhodin (*K. Landt. Akad. Handl.*, 1888, 37, 25), in experiments with emulsified oils also observed an increase of milk fat, followed by a fall to the normal amount.

The examination of the milk of cows fed with rations containing different amounts of fat (compare preceding abstract) showed a very decided increase in the percentage of fat in milk during the first two weeks of the period in which a ration rich in fat was fed; in the third week of the same period, the percentage of milk fat diminished. The following are the percentages of fat found each week. Period I (digestible fat, 0.36 lb. per day): (1) 5.34, (2) 5.21, (3) 5.66, (4) 5.94. Period II (0.86 lb. fat): (5) 6.39, (6) 6.43, (7) 6.05, (8) 6.15. Period III (0.55 lb. fat): (9) 5.64, (10) 5.78, (11) 5.96, and (12) 5.74. The decrease of milk-fat in the third period is attributed to the gradual return of the cows to their normal capacity.

N. H. J. M.

Effect of Emulsified or Non-emulsified Fat on [Milk] Production. By JOSEF L. HILLS (12th Ann. Rep. Vermont Agr. Expt. Stat. for 1898—1899, 269—275).—From the results of two years' experiments the following conclusions are drawn. Addition of cotton seed, maize, or linseed oils tends to increase the yield of milk per unit of dry matter consumed. With cotton seed oil there seems to be a fairly permanent increase of 0.2—0.3 per cent., in the fat of the milk, but maize and linseed oils, when fed as a regular diet, seem to lower the percentage of fat, although, when first given, all the oils produced marked gains in milk fat. The improvement in the quality of the milk under the influence of cotton seed oil took place both with emulsified oil and oil which had not been emulsified.

By feeding with oil, the butter is injured to an extent which far outweighs any possible benefit from increased yield and quality (compare following abstract).

N. H. J. M.

Effect of Food on the Quality of Butter. By JOSEF L. HILLS (12th Ann. Rep. Vermont Agr. Expt. Stat., 1898—1899, 296—298. Compare this vol., ii, 236).—The rations contained hay and usually silage besides cotton seed, linseed and maize meals, and bran, in two different combinations; maize meal and bran; maize meal, bran, and buckwheat middlings; Buffalo gluten feed; Tucker oat feed. At times emulsified cotton seed, maize, and linseed oils were added to the maize and bran ration. The following average results were obtained with the butter:

Without oil.			Maize oil.			Cotton seed oil.			Linseed oil.		
Vola- tile acids.	Iodine num- ber.	M. p.	Vola- tile acids.	Iodine num- ber.	M. p.	Vola- tile acids.	Iodine num- ber.	M. p.	Vola- tile acids.	Iodine num- ber.	M. p.
29.3	28.0	33.8°	17.8	44.7	34.3°	23.2	39.8	36.4°	20.2	47.8	34.1°

The effects of the oil, especially maize and linseed oil, were maintained for some time after the oil was discontinued. The cotton seed butter was hard and of good quality, the linseed butter very soft and sticky, whilst the maize oil butter was rather soft and oily, but of fair quality.

It is hardly safe to conclude that the oils actually migrate to the milk, but the results lend support to this view. N. H. J. M.

Composition and Food-value of the Salt Bushes. By MEJER E. JAFFA (*Univ. California Agr. Expt. Stat. Bul.*, 125, 1899, 24—30).—The percentage composition of two samples of *Atriplex semibaccata* grown at Tulare and Paso Robles was found to be as follows:

	Water.	Crude proteid.	N-free extract.	Crude fat.	Crude fibre.	Pure ash.
1.	78.03	2.75	10.41	0.48	3.75	4.58
2.	75.00	3.93	10.15	0.41	5.58	4.93

As regards digestibility, feeding experiments are required. In the meantime, the author would assign to the hay about the same digestive coefficients as for oat hay. Salt bushes should not be fed alone, owing to the high percentage of saline ingredients, and should be given in gradually increasing amounts. Sheep and cattle have, however, been fed exclusively with the material throughout an entire season.

The composition of the ash (of 1) is as follows:

Na ₂ O.	K ₂ O.	CaO.	MgO.	Fe ₂ O ₃ .	Al ₂ O ₃ .	Mn ₂ O ₄ .	P ₂ O ₅ .	SO ₃ .	SiO ₂ .	Cl.
35.39	11.42	5.79	3.23	1.38	1.95	0.22	2.80	2.64	16.24	24.33

Although the percentages of potash and phosphoric acid are low, the actual amounts are much greater than those yielded by an ordinary crop of hay. N. H. J. M.

Edible Earth from Fiji. By B. G. CORNEY, DAVID, and FREDERICK B. GUTHRIE (*Journ. and Proc. Roy. Soc. N.S. Wales*, 1900, 33, 224—227).—The sample of soil was obtained from the Island Vanua Levu, and consists of a very soft, pale pink, clayey material with small, white patches, and lumps of grey to reddish chalcedony. It contained a good many quartz crystals and numerous small, octahedral crystals of magnetite. It therefore seems likely that the rock was originally a quartz andesite (dacite), probably of tuffaceous origin. The following analytical results are given:

Loss at 120°.	Combined water.	Al ₂ O ₃ .	Fe ₂ O ₃ .	SiO ₂ .
2.45	12.78	41.53	7.66	35.09

The substance contains no lime or magnesia, and would seem to be a silicate of the formula $\text{Al}_2\text{O}_3(\text{SiO}_2)_2(\text{H}_2\text{O})_2$, with ferric oxide as impurity. N. H. J. M.

Basic Constituents of Crops. By ROBERT WARINGTON (*Agr. Students' Gaz.*, 1899, [ii], 9, 133—138).—The author remarks that he had previously pointed out that the carbonates found in plant ashes must be in part a residue of nitrates. The bases of the nitrates remain, after the nitric nitrogen has been utilised by the plant, and probably become united with organic acids.* The results of calculations of the lime corre-

* Compare Lawes and Gilbert (*Journ. Roy. Agric. Soc. Eng.*, 1894, [iii], 5, 636—641; *Proc. Roy. Soc.*, 1899, 65, 329—332; and *Phil. Trans.*, 1900, 192, B., 150—174).

sponding with the whole of the nitrogen of various crops, and of the amounts of lime equivalent to the bases of the ash, after satisfying the phosphoric (assumed to be dibasic) and hydrochloric acids present, showed, in every case, with the exception of mangels, a great deficiency of bases on the assumption that most of the nitrogen enters into the plant in the form of nitrate. The results of Arendt's experiments with oat-plants which were analysed at different dates, from June 10 to July 31, showed a falling off in the salifiable base as percentage of nitrate base from 41—44 to 27.

Unless, therefore, cereals take up only about a quarter of their total nitrogen in the form of nitrates, it must be assumed, as is probably the case, that a loss of bases occurs. The differences in the amount and composition of barley straw harvested at Rothamsted in wet and dry seasons, indicated that losses occur owing to the washing out of withered stems and leaves in wet weather. There is probably also a loss of ash-constituents by diffusion into the soil, especially when the crop ripens and the sap becomes more and more concentrated. The diffusion into the soil would occur chiefly during the night.

N. H. J. M.

[Basic Constituents of Crops.] By EM. DEMOUSSY (*Ann. Agron.*, 1900, 26, 251—257).—With reference to the preceding paper, it is pointed out that, although plants do not take up much nitrogen in the form of ammonia, since the soil generally contains very little, any ammoniacal nitrogen taken up would further increase the deficiency of base by leaving the acid of the ammonium salt in the plant.

The deficiency of bases in plant ashes is attributed partly to a certain amount of nitrogen being taken up in other forms than nitrate, especially as organic compounds, and partly to losses in dead leaves both attached and fallen. The results of experiments with wheat showed that losses of dry matter, greater losses of total ash, and still greater losses of potash took place in July (compare Dehérain and Bréal, *Abstr.*, 1882, 419; Rouf, "Étude anal. sur la canne à sucre," *La Martinique*, 1879, and Dehérain, *Ann. Agron.*, 1879, 5, 271).

The possibility of losses of ash constituents by diffusion into the soil when the concentration of the sap increases was suggested by Marie-Davy and Albert Lévy (*Ann. Montsouris*, 1873 and 1876), but the results of experiments by the author and others indicate that living portions of plants retain with great vigour all the mineral matter absorbed. Knop's results were probably due to mutilated plants having been employed (compare *Abstr.*, 1894, ii, 153).

N. H. J. M.

Manurial Experiments with Fruit Trees. By STEGLICH (*Bied. Centr.*, 1900, 29, 292—296; from *Mitt. Deut. Landw. Ges.*, 1897, No. 4, 39).—The percentage amounts of food constituents in fruit trees increase from the root-wood to the fruit-wood, and are still greater in the leaves. The amount of nitrogen in the vegetative organs is always greater than that of the potash.

The yearly amounts of nitrogen, potash, lime and phosphoric acid required by fruit trees with stems 25 cm. in circumference have been estimated. The following results are given (in grams) for apple, pear,

cherry, and plum trees : N, 59, 37, (76) and (34) ; K_2O , 51, 40, 95, and 74 ; CaO , 109, 69, 209, and 75 ; P_2O_5 , 11, 7, 30, and 11. Provisional estimates were made of the manurial requirements of fruit trees for each cm. of circumference.

A large number of measurements and weighings have been made, the results of which show the relations of the amounts of total wood to the amount of stem wood, the average increase in circumference per annum, and the relation of the amount of foliage to the circumference of the trees, &c.

N. H. J. M.

Storage of Stable Manure. By FRIEDRICH HOLDEFLEISS (*Mitteil. Landw. Inst. kgl. Univ. Breslau*, 1900, Heft. 3, 49—55).—Three samples of manure from previous experiments (*ibid.*, Heft. 2) were employed. They contained 6415, 5532, and 5480 grams of total nitrogen respectively ; 7.35, 3.61, and 2.05 per cent. of the nitrogen were in the form of ammonia, and 88.2, 88.3, and 92.3 per cent. were in the form of proteids. The three lots were kept (1) without preservative, (2) with potassium salt, and (3) with superphosphate.

The percentage losses or gains of the different constituents were as follows :

	N.	N as NH_3 .	Proteid N.	Non-proteid organ. N.	Non-nitrog. extract.	Crude fibre.	Pentosans.
1.	- 18	- 64	- 20.3	+ 105	- 8.7	- 27.5	- 35.1
2.	- 6.3	+ 48	- 11.3	+ 32	- 27.5	- 6.9	- 16.7
3.	- 6.75	+ 306	- 14.1	no change	- 27.5	- 9.4	- 22.5

As regards nitrogenous constituents, the effect of preservatives was not only to diminish the loss of proteid nitrogen, but to increase considerably the amount of nitrogen in the form of ammonia.

Of the non-nitrogenous constituents, the pentosans and non-nitrogenous extract are the substances which decomposed most readily. In crude fibre *minus* pentosans there was only a loss in (1) amounting to 17.5 per cent. ; in (2) and (3) there were gains of 7.6 and 7.9 per cent.

N. H. J. M.

Analytical Chemistry.

Burette for Accurate Gas Analysis. By ALFRED H. WHITE (*J. Amer. Chem. Soc.*, 1900, **22**, 343—349).—This is an improvement on the Hempel-Petterson apparatus. For working particulars, reference must be made to the original with its five illustrations.

The main body of the burette consists of 12 bulbs, each with a capacity of about 12 c.c. A line is etched on each constriction and the capacity of the bulb between these marks is determined; no reading telescope is required, yet the volume of the gas may be read off within 0.02 c.c.

The other parts of the apparatus, which is enclosed in a water-jacket, consist of a side burette and of a manometer placed below

a specially constructed stopcock which prevents the escape of gas or entrance of outer air when connection is made with the absorption pipettes.

The burette in which mercury is employed compensates automatically for all changes of temperatures and pressure. L. DE K.

Alkalimetry and Acidimetry in Volumetric Analysis. By A. ASTRUC (*Compt. rend.*, 1900, 130, 1636—1639).—The author summarises and discusses the various observations which have been made on the behaviour of phenols, amines, organic acids, and other carbon compounds with various indicators. C. H. B.

New Methods of Mineral Analysis. By ADOLPHE CARNOT (*Ann. des Mines*, 1898, [ix], 14, 113—209).—A collection is given of 21 methods which have previously been published separately (*Abstr.*, 1898, ii, 349, &c.). L. J. S.

Iodometric Estimation of Hydrogen Peroxide, Alkali Percarbonates and Persulphates. By ERWIN RUPP (*Arch. Pharm.*, 1900, 238, 156—158).—Hydrogen peroxide may be estimated with great accuracy by adding 1 c.c. of the sample to 20 c.c. of water mixed with 5 c.c. of dilute sulphuric acid and 1 gram of potassium iodide. After being kept for half an hour in a closed flask, the liberated iodine is titrated, as usual, with *N*/10 sodium thiosulphate. Percarbonates may be estimated in a similar manner. The process is also applicable to persulphates, but the time of reaction should be extended to 2 hours. L. DE K.

Detection of Fluorine in Wine. By GIULIO PARIS (*L'Orosi*, 1900, 23, 1—3).—The ignited ash from 50 c.c. of the wine is mixed in a platinum crucible with one-third of its weight of precipitated silica and about 0.5 c.c. of concentrated sulphuric acid. The lid of the crucible, on the bottom of which is suspended a drop of distilled water, is then put on and a little ice placed on the upper surface. After heating the crucible with a very small flame for about 5 minutes, it is allowed to cool and the drop of water hanging from the lid is removed to a microscope slide, a small portion of which is covered with a thin uniform coating of Canada balsam. A few small crystals of sodium chloride are then added and after a lapse of half an hour to an hour the slide is examined under the microscope; if the wine contains fluorine, hexagonal crystals of sodium silico-fluoride are observable. T. H. P.

Estimation of Ozone. By OTTO BRUNCK (*Ber.* 1900, 33, 1832—1842. Compare Ackermann, *Chem. Zeit.*, 1900, 24, 235).—In the estimation of ozone by the liberation of iodine from potassium iodide solution, trustworthy results can only be obtained when the solution is treated with the theoretical amount of sulphuric or acetic acid necessary to liberate hydrogen iodide. When a neutral solution of potassium iodide is employed, the amount of ozone always comes too low, probably owing to the formation of potassium peroxide which destroys part of the iodine and also to the interaction of ozone and hydrogen peroxide. In acid solutions, a slight error occurs when very

concentrated solutions are employed, owing to decomposition of the hydriodic acid, but this may be eliminated by making a blank determination.

J. J. S.

Selenium and Tellurium. By EDWARD KELLER (*J. Amer. Chem. Soc.*, 1900, 22, 241—245. Compare Abstr., 1898, ii, 638).—*Quantitative Separation of Selenium and Tellurium.* The method is based on the fact that selenious acid dissolved in strong hydrochloric acid is reduced by sulphur dioxide; any tellurous acid may then be reduced by adding water and boiling. The process has been derived more particularly for the analysis of crude copper.

One hundred grams of copper with 2—4 grams of ferrous sulphate are dissolved in 400 c.c. of nitric acid (sp. gr. 1.42), the nitrous fumes expelled, and the solution diluted, cooled, and mixed with sufficient ammonia to redissolve the copper precipitate. After boiling and settling, the ferric hydroxide containing the selenium and tellurium is collected on a filter; as it always retains copper, it must be repeatedly redissolved in acid and reprecipitated with ammonia. The precipitate is then dissolved in just sufficient hydrochloric acid, saturated with hydrogen sulphide, and the precipitated sulphide after being well washed is digested with sodium sulphide, which dissolves the sulphides of selenium and tellurium. The filtrate is carefully acidified with nitric acid and evaporated to dryness; the residue now contains the dioxides of selenium and tellurium, besides sodium nitrate and some sulphur. Two hundred c.c. of strong hydrochloric acid are added and the whole is boiled until all nitro-hydrochloric acid is expelled and the two elements have been reduced to the lower state of oxidation. When cold, the liquid is passed through a Gooch filter and the residue washed with strong hydrochloric acid. A current of sulphur dioxide is now passed through the solution to precipitate the selenium which is washed first with dilute hydrochloric acid, then with water, and finally with alcohol, and is then dried and weighed. The filtrate containing the tellurium is diluted with an equal bulk of water and boiled to precipitate the tellurium, more sulphur dioxide being passed if necessary. It is then collected and treated in the same manner as the selenium. The results are quite satisfactory, notwithstanding Lenher's assertions that small quantities of selenium cannot be accurately estimated in the presence of much tellurium; the amount of hydrochloric acid should, however, be about 100 times that of the tellurium.

L. DE K.

Distillation of Ammonia in the Estimation of Nitrogen. By FRANCIS GANO BENEDICT (*J. Amer. Chem. Soc.*, 1900, 22, 259—263).—When distilling dilute solutions of ammonia, this is generally expelled in a very short time, but still it is necessary to keep on distilling a considerable volume in order to wash out the ammonia adhering to the condensing tube. If the latter is not cooled, the ammonia is very soon expelled, but this causes other inconveniences, such as the possible overheating of the standard acid into which the ammonia is received.

The author now combines the two methods. The vapour passes through a vertical tin condensing-tube fixed into a galvanised iron tank filled with water, which may be drawn off by means of a tap. When the bulk

of the ammonia is supposed to have passed over, the refrigerating water is slowly withdrawn, thus allowing the tube to get hot.

L. DE K.

Rapid Method for the Estimation of Carbon in Iron or Steel by Combustion. By GEORGE W. SARGENT (*J. Amer. Chem. Soc.*, 1900, 22, 277—285).—This is a modification of the ordinary process of burning the carbonaceous residue of iron or steel in a current of air or oxygen. The air or oxygen employed is first passed over a red-hot spiral made from a platinum tube 17 inches long and $\frac{5}{32}$ inch in diameter; this gives four close coils $\frac{3}{4}$ inch in diameter, and leaves 4 inches extended on either side. The object is to fully oxidise any hydrocarbons which may be present in the air, and the carbon dioxide formed is then absorbed in a Geissler bulb apparatus. The carbon is placed in a porcelain boat heated inside a porcelain combustion tube and the resulting gases are passed through a tube containing red-hot copper oxide to insure complete oxidation. It has been found that the same object is attained by passing the gases through a small glass tube in which two platinum wires were fused, so that a spark would be produced between the points, when a current from a Rhumkorff coil passed through the wires. As there is, however, always a danger of stoppage, the use of copper oxide is the safest. To retain traces of hydrochloric acid or chlorine, the gases are afterwards passed through a $\frac{1}{2}$ -inch glass tube 6 inches long, containing loosely-packed coarse wet sand held in place by two small discs of copper gauze placed at either end.

Precautions are taken to prevent overheating of the corks. The dried gases are then finely absorbed in a weighed Geissler apparatus of somewhat larger size than usual, and containing 30 c.c. of aqueous caustic potash of sp. gr. 1.27.

L. DE K.

Estimation of Carbon in Steel. By GEORGE AUCHY (*J. Amer. Chem. Soc.*, 1900, 22, 334—343).—The method of estimating the carbon by igniting the carbon sponge, and attributing 70 per cent. of the loss in weight to the presence of carbon, is said to be untrustworthy. No better results are obtained by treating the carbon sponge with nitric acid.

The colour tests are also untrustworthy, the same sample giving sometimes a difference of 0.1 per cent. of carbon.

Sources of error are pointed out in the moist and dry combustion process; as regards the latter, Shimer's apparatus will, in the author's opinion, eventually displace the old arrangement.

L. DE K.

Estimation of Carbon and Sulphur in Steel. By BERTRAM BLOUNT (*Analyst*, 1900, 25, 141—144).—The author has attempted to estimate carbon and sulphur in iron by direct combustion in pure oxygen. The sample is heated at about 1200° in a porcelain boat contained in a porcelain tube, and the products of combustion are passed into suitable absorbents. The process does not answer well for sulphur, and even for carbon it is not as yet preferable to the existing methods. It might be made more generally applicable if

means were found to completely oxidise the iron at a temperature not exceeding 800°.

L. DE K.

Estimation of Alkali Carbonates in Presence of Alkali Hydrogen Carbonates. By FRANK K. CAMERON (*Amer. Chem. J.*, 1900, 23, 471—486).—Alkali carbonates interact with potassium hydrogen sulphate to give sodium hydrogen carbonate and sodium potassium sulphate; since both the latter are neutral to indicators, the carbonates can be separately estimated by adding a standard solution of the acid sulphate until the pink coloration of the phenolphthalein disappears; the hydrogen carbonates are, however, unstable, and gradually decompose into carbonates and carbon dioxide. Salts of other weak acids, such as the borates, silicates, and phosphates, can be similarly estimated.

The hydrogen carbonates do not yield a CO_3 ion, except by decomposition into carbonates, and do not themselves precipitate silver salts; chlorides can therefore be titrated directly against silver nitrate in presence of hydrogen carbonates, if the decomposition of the latter is prevented by a very slight excess of acid sulphate.

T. M. L.

Estimation of Calcium and Sulphuric Acid by the Photometric Method. By J. I. D. HINDS (*J. Amer. Chem. Soc.*, 1900, 22, 269—274).—The author has extended his process (*Abstr.*, 1896, ii, 574) to the estimation of calcium in limestone. About 0.10 of the sample is dissolved in hydrochloric acid and a few drops of nitric acid, and evaporated to dryness over a free flame. The residue is dissolved in water with a little hydrochloric acid, neutralised with ammonia diluted to 150 c.c., and mixed with a little solid ammonium oxalate. The turbid liquid is then poured into the apparatus previously described until the image of the candle flame just disappears. The depth is read and the percentage of calcium in the liquid is calculated from the equations:

For calcium carbonate, $y = 0.0642/x - 0.3$; for calcium oxide, $y = 0.0360/x - 0.3$, in which x is the reading of the cylinder in cm. and y the percentage sought.

The percentage of calcium in the sample is then found by an easy calculation.

Small quantities of sulphuric acid in liquids may be similarly estimated by adding solid barium chloride and using the equations:

For H_2SO_4 , $y = 0.0590/x$; for SO_3 , $y = 0.0482/x$.

Tables are given to save the trouble of calculating.

L. DE K.

Estimation of Zinc by the Use of Standard Thiosulphate Solution. By RICHARD K. MEADE (*J. Amer. Chem. Soc.*, 1900, 22, 353—356).—The author recently proposed a new volumetric process for the estimation of magnesium (this vol., ii, 48), and has applied the same principle to the estimation of zinc. The strongly ammoniacal solution is mixed with sodium arsenate, and any precipitate due to calcium, magnesium, &c., is filtered off. The filtrate is nearly neutralised with nitric acid and then faintly acidified with acetic acid. After being washed, the precipitated zinc arsenate is dissolved in

dilute hydrochloric acid, potassium iodide added, and the liberated iodine titrated with standard sodium thiosulphate, addition of starch being superfluous.

Manganese, which is frequently present in zinc ores, must be first removed by treating the sample with nitric acid and potassium chlorate.

L. DE K.

Quick and Exact Test for Mercury in Urine. By ADOLF JOLLES (*Monatsh.*, 1900, 21, 352—360; *Zeit. anal. Chem.*, 1900, 39, 230—237).—The urine (100—150 c.c.) acidified with concentrated hydrochloric acid (5—10 c.c.) is heated with potassium chlorate (1.5—2 grams) until it no longer smells of chlorine, and then mixed with a dilute solution of stannous chloride; in this mixture, a gilt platinum foil is placed for 15 minutes; the foil is then treated with nitric acid and the solution evaporated to a small bulk and tested with stannous chloride or hydrogen sulphide. It is thus possible to detect 0.000066 gram of mercury in 100 c.c. of urine. A quantitative method is based on the same test, the yellow coloration produced by hydrogen sulphide in the dilute mercury solution being compared with that of solutions of known strength.

R. H. P.

Separation and Estimation of Mercury as Mercurous Oxalate. By C. A. PETERS (*Amer. J. Sci.*, 1900, [iv], 9, 401—406).—Mercury in solution as mercurous nitrate may be estimated volumetrically by adding a known weight of ammonium oxalate and titrating the excess of oxalic acid in the filtrate with standard solution of potassium permanganate. An attempt to estimate the oxalic acid in the precipitate proved unsuccessful.

In solutions containing from 2—5 per cent. of excess of nitric acid (sp. gr. 1.15), mercurous salts may be quantitatively separated from mercuric salts if the latter do not exceed 20 per cent. of the total mercury.

Instead of estimating the mercurous compound volumetrically, the precipitated mercurous oxalate may be weighed as such. As it is not stable at 100°, however, it should be collected on a weighed asbestos filter and dried over sulphuric acid to constant weight, which is generally accomplished in about 15 hours if the weight does not exceed a few decigrams.

L. DE K.

Estimation of Cerium. By GEORG VON KNORRE (*Ber.*, 1900, 33, 1924—1929. Compare Abstr., 1898, ii, 311; *Job*, Abstr., 1899, ii, 334).—Cerium in ceric salts may be readily estimated by reduction with excess of hydrogen peroxide and subsequent estimation of the excess of peroxide by standard permanganate. Hitherto, no good method has been described for the oxidation of cerous to ceric salts; the author finds, however, that extremely dilute solutions of cerous compounds which have been acidified with the smallest possible amount of sulphuric acid are readily oxidised by boiling for a few minutes with ammonium persulphate; the change in colour, from colourless to yellow, is very characteristic, and may possibly be the most delicate test for cerium. The subsequent estimation of the ceric compound is carried out as just described.

J. J. S.

Estimation of Alumina and Ferric Oxide in Natural Phosphates. By F. P. VEITCH (*J. Amer. Chem. Soc.*, 1900, 22, 246—258).—*Estimation of Alumina.*—One gram of the substance is treated in a platinum dish with 5—10 c.c. of hydrofluoric acid and after 2 or 3 hours the solution is evaporated to dryness on the water-bath; 2 c.c. of sulphuric acid are added, and the whole gently heated until the substance no longer flows in the dish. When cold, 10—20 c.c. of hydrochloric acid are added, and after warming a few minutes to soften the mass this is transferred to a small beaker and boiled for 15—30 minutes to dissolve all aluminium compounds. The liquid is then diluted and passed through a filter and the undissolved matter is well washed. To the filtrate are added 50 c.c. of a 25 per cent. solution of ammonium chloride, then ammonia until alkaline, and then enough hydrochloric acid to just redissolve the precipitate. When cold, the mixture is diluted to about 250 c.c., and a 50 per cent. solution of ammonium thio-sulphate is added drop by drop until the solution is colourless, adding in all 20 c.c.; the beaker is covered with a watch glass and the mixture is boiled for half an hour. The precipitate, after being drained, is washed back into the same beaker, redissolved in hydrochloric acid, mixed with 2 c.c. of a 10 per cent. solution of ammonium phosphate, and reprecipitated in the way described. The aluminium phosphate is washed 20 times with a 5 per cent. solution of ammonium nitrate and ignited over the blowpipe to constant weight.

Estimation of Ferric Oxide.—One gram of the substance is heated with 20 c.c. of sulphuric acid. The mixture is diluted with water and filtered; should organic matter be suspected, the solution is boiled for some time with addition of a little potassium chlorate. The mixture is then reduced with zinc in the ordinary way, and titrated with a standardised solution of potassium permanganate.

Part of the paper is devoted to a criticism of existing methods.

L. DE K.

Preparation of Potassium Xanthate for Nickel Estimations. By EDWARD D. CAMPBELL (*J. Amer. Chem. Soc.*, 1900, 22, 307—308. Compare Abstr., 1895, ii, 421).—As commercial potassium xanthate is often not sufficiently pure, it is advisable to prepare the salt specially. Fused potassium hydroxide is placed in a tightly stoppered flask and covered with absolute alcohol, of which 2.5 c.c. should be used for each gram of the hydroxide. When dissolved, the liquid is poured off from any undissolved carbonate into a beaker which is placed in ice-water until the temperature is reduced to 10° or less, and carbon disulphide is gradually added with constant stirring, using 1 c.c. for each gram of potassium hydroxide. The crystalline mass is collected on a Buchner funnel, using the suction-pump, washed once with a very little absolute alcohol, and then twice with a little ether. When properly dried at about 100°, the compound will keep for years.

L. DE K.

Colorimetric Estimation of Vanadium. By LOUIS MAILLARD (*Bull. Soc. Chim.*, 1900, [iii], 23, 559—563).—The method described is adapted for the estimation of small quantities of vanadium, and is

based on the red coloration, probably due to the formation of a per-vanadic acid, produced by the action of hydrogen peroxide on vanadic acid. 10 c.c. of the liquid under examination are placed in a graduated cylinder, 1—5 c.c. of hydrochloric acid and 3—10 c.c. of an ethereal solution of hydrogen peroxide added, the mixture well agitated, and water added until the aqueous layer measures 15 c.c. The operation is repeated with 10 c.c. of a 0.1 per cent. solution of sodium vanadate, and the two liquids examined and compared in a colorimeter. Experiments are cited to prove that the intensity of the coloration is strictly proportional to the amount of vanadic acid present, and is not affected by excess of acid and hydrogen peroxide, or by the presence of various salts. N. L.

Electrolytic Estimation of Bismuth. By DMITRY BALACHOWSKY (*Compt. rend.*, 1900, 131, 179—182).—An adherent deposit of bismuth, suitable for quantitative estimations, may be obtained by working with feeble currents (maximum current density $ND_{100} = 0.06$ ampere), roughened electrodes, and slightly acidic solutions, free from large quantities of haloid salts.

About 0.6 gram of the sulphate or nitrate, mixed with 3—4 grams of carbamide, and dissolved in 5—6 c.c. nitric acid, diluted with 150 c.c. of water, are electrolysed in a roughened Classen capsule for 6—8 hours at 60°, with a current density of 0.03—0.04 ampere, and a difference of potential 1.5—1.9 volts; towards the close of the electrolysis, the current density is increased to 0.08 ampere, and the E.M.F. to 2 volts.

Formaldehyde or acetaldehyde may be added instead of carbamide, and in this case the operation is finished by warming to 80—90°, and slightly decreasing the voltage and current density.

The precipitated metal is washed without stopping the current, and dried at 100°; the deposit is readily removed from the capsule by the action of nitric acid. The analytical results are exhibited in tabular form. G. T. M.

Bismuth Cobalticyanide. By JOHN A. MATHEWS (*J. Amer. Chem. Soc.*, 1900, 22, 274—277).—Further particulars are given about the constitution and properties of bismuth cobalticyanide (this vol., ii, 318). The results have not been favourable to the proposed use of potassium cobalticyanide in the analysis of pig-leads, but the salt may be used in the analysis of regular lead-bismuth alloys. It has been found that unless 1 c.c. of the liquid contains at least 0.0079 gram of bismuth, the precipitation is not complete in any circumstances. As a rule, the precipitation is favoured by operating at the boiling heat; once a precipitate is formed, it does not redissolve even in a quantity of water, which would have prevented its formation at the beginning. A large excess of the reagent also increases its insolubility, also the presence of free acetic acid. Bismuth cobalticyanide is crystalline, settles and filters well, and does not completely give up its water below 165°. The formula of the dry compound is $\text{BiCo}(\text{CN})_6$. When freshly thrown down, the precipitate looks white, but on the filter it acquires a greenish tint, which, on drying, changes

to blue ; on exposure to the air, it reabsorbs water and assumes a pink colour.

L. DE K.

Determination of the Hardness of Water. By GIUSEPPE VENTUROLI (*L'Orosi*, 1900, 23, 39—43).—To obviate the inconveniences of the Clark method and its modifications for determining the hardness of water, the following process is recommended. 40 c.c. of the water are acidified with hydrochloric acid and evaporated to dryness, the residue being dissolved in distilled water, and the solution mixed with a measured volume (50 to 60 c.c.) in excess of standard sodium carbonate solution (0.429 gram of Na_2CO_3 per litre). After heating to boiling and adding methyl-orange (or another indicator), the excess of sodium carbonate present is determined by titration with an acid solution of strength equivalent to that of the sodium carbonate solution. This gives the total hardness, each c.c. of the sodium carbonate solution corresponding with 1 part of calcium carbonate per 100,000 parts of water. To obtain the separate proportions of lime and magnesia in the water, it is necessary to determine, besides the total hardness, (1) the hardness after the calcium salts have been precipitated with ammonium oxalate solution, this giving the total amount of magnesia ; (2) the hardness after the water has been boiled, representing the lime and magnesia not combined with carbonic acid ; (3) the hardness after the removal of the calcium salts from the boiled water by means of ammonium oxalate, this giving the amount of magnesia not in combination with carbonic acid.

T. H. P.

West Indian Sandalwood Oil. By ERNST DEUSSEN (*Arch. Pharm.*, 238, 149—156. Compare *Abstr.*, 1899, i, 924 ; this vol., i, 242, 401).—This oil may be identified by the large amount of santalol it contains. The percentage of this alcohol in sandalwood oil may be calculated from the equation $P = a \times 22.2/s - (a - 0.42)$, in which a represents the number of c.c. of normal alkali consumed, and s the number of grams of the acetylated oil used in the experiment. As the constitution of this oil is but little known, the author has subjected a genuine sample to fractional distillation, analysis and further research.

The oil boils at 265° under atmospheric pressure, undergoing slight decomposition, but on distilling under 23 mm. pressure 6 fractions were obtained, boiling respectively at 139 — 147° , 147 — 155° , 155 — 160° , 160 — 168° , 168 — 171° , and 171 — 174° , a small quantity of resinous matter remaining in the flask. Most of the oil was contained in fractions 2, 4, and 6. Of these, 2 and 4 were subjected to ultimate analysis, and their molecular weight was determined by the freezing point method ; the results obtained showed that these fractions probably contain a mixture of a sesquiterpene alcohol and a sesquiterpene.

By treating a solution of the oil in twice its volume of dry ether with hydrogen chloride, bromide, or iodide, crystalline compounds were obtained which chemically and physically corresponded with those of cadinene. There is, therefore, little doubt that sandalwood oil contains cadinene, the amount being about 16 per cent.

L. DE K.

Valuation of Spirit of Camphor. By ALFRED PARTHEIL and A. VAN HAAREN (*Arch. Pharm.*, 1900, 238, 164—166).—See this vol., i, 507.

Assay of Creosote. By A. D. HALL (*Analyst*, 1900, 25, 148—151).—One hundred c.c. of the sample are put into a distilling flask and the measuring flask is rinsed with 5 c.c. of benzene which are afterwards deducted from the volume of the distillate. After distilling until nothing more comes over at 325° , the volume of the distillate is read off. This is then shaken with 100 c.c. of sodium hydroxide solution of sp. gr. 1.2 or 1.3, and the mixture put in a water-oven for at least 1 hour, being shaken from time to time; when cold, the volume of the alkaline solution is read off and the greater part is withdrawn by means of the tap attached to the graduated cylindrical receiver.

The soda solution is boiled for a few minutes to expel hydrocarbons. When cold, 10 c.c. are withdrawn by a pipette and introduced into a Leffmann-Beam milk bottle (specially calibrated for the purpose); dilute sulphuric acid is added to neutralise the alkali, and the bottle whirled in the machine for a few minutes. When cold, the volume of the tar acids is read off.

To the contents of the receiver 100 c.c. of dilute sulphuric acid (1:5) are now added, and the whole is heated and shaken as before. The volume of the acid is then read off and 10 c.c. are mixed with excess of alkali in a milk bottle, which on being whirled causes the liberated tar bases to collect in the neck, when their volume may be read off.

Technical experiments not yet concluded seem to point to the fact that the pyridine tar bases are quite as valuable for preservative purposes as the tar acids. L. DE K.

Volumetric Valuation of Syrup of Ferrous Iodide. By ERWIN RUPP (*Arch. Pharm.*, 1900, 238, 159—160).—The process is based on the fact that on adding potassium permanganate to an acid solution of ferrous iodide the iodine is liberated. On adding potassium iodide, this dissolves and at the same time a further amount of iodine is liberated by the action of the ferric salt on the potassium iodide; the iodine may then be titrated with sodium thiosulphate. When dealing with syrup of ferrous iodide, the unavoidable excess of permanganate is rapidly decomposed by the sugar.

Five grams of the syrup, 5—10 c.c. of water, and 10 c.c. of dilute sulphuric acid are introduced into a 100 c.c. stoppered bottle and a 1 per cent. solution of potassium permanganate is slowly added until the liquid remains pink for a few seconds. After 3 hours, one or two grams of potassium iodide are added, and after remaining in the dark for another hour, the liberated iodine is titrated with $N/10$ sodium thiosulphate, using starch as indicator. A 5 per cent. solution of ferrous iodide consumes 24.2 c.c. of $N/10$ sodium thiosulphate.

L. DE K.

Relation of the Reducing Power of Normal Urine to the Amount of Certain Nitrogen Compounds Present. By JOHN H. LONG (*J. Amer. Chem. Soc.*, 1900, 22, 309—327).—The copper solution used

in the experiments was prepared by dissolving in water 8.166 grams of crystallised copper sulphate, 15 grams of 100 per cent. sodium hydroxide, 25 c.c. of glycerol, 350 c.c. of ammonia of sp. gr. 0.9 and diluting to 1 litre. Fifty c.c. are diluted with 50 c.c. of water and boiled in the well-known Pavy apparatus; to prevent too rapid an escape of ammonia, some paraffin wax is added, also a few fragments of pumice-stone, and the burette tip for discharging the sugar solution or the urine is made long enough to pass down the neck of the flask and below this paraffin. If the saccharine solution contains 0.2 per cent. of dextrose, then 1 mol. of this will reduce exactly 5.88 mols. of copper oxide. Using this solution with uric acid and creatinine, it was found that 1 mol. of the former reduces 2.98 and 1 mol. of the latter 1.998 mols. of copper oxide. Processes are given for the estimation of these substances in urine so as to be able to allow for their reducing power when estimating the reducing power of a sample of urine. This reducing power is larger than that caused by uric acid and creatinine, proving the presence of normally existing sugar and, possibly, other reducing substances.

Estimations of urea by the mercury and hypobromite methods and its relation to the uric acid are also given.

L. DE K.

Estimation of Glycogen. By EDUARD PFLÜGER (*Pflüger's Archiv*, 1900, 80, 351—369, 527—532; 81, 1—7. Compare Abstr., 1899, ii, 529, 819).—Largely polemical. Austen's method of estimating glycogen consists in a preliminary digestion of the substance with Finkelberg's pepsin, and subsequent treatment according to Külz's method. The pepsin used, however, contains a variable amount of glycogen or a similar polysaccharide; the glycogen obtained contains nitrogen, and a loss of glycogen occurs in prolonged peptic digestion. The final result is too low. A protest is entered against the incomplete and incorrect account of the Pflüger-Nerking method given in Salkowski's recently published text-book. A number of new experiments are given to show that this method is the best at present in vogue.

W. D. H.

Estimation of Chloral Hydrate and Chloroform in Toxicological Analysis. By CARL KIPPENBERGER (*Arch. Pharm.*, 1900, 238, 81—100).—When chloral is distilled with an alkali, a not inconsiderable portion of the chloroform formed is decomposed according to the equation $\text{CHCl}_3 + 3\text{KHO} = 3\text{KCl} + 2\text{H}_2\text{O} + \text{CO}$. The author now estimates this carbon monoxide by taking advantage of its reducing action on palladium chloride.

The material to be tested is, if necessary, rendered faintly acid, then mixed with a fairly large quantity of magnesium oxide and introduced into a distilling flask placed in a water-bath. The flask is provided with a doubly-perforated cork, one opening of which is connected by means of an india-rubber tube and clamp with a Woulf's bottle containing aqueous caustic potash. This arrangement allows of the transmission of air later on. Through the other opening passes a tube connected with a small condenser which in turn is connected with another Woulf's bottle, then with a wash bottle containing dilute hydrochloric acid, and finally with a Lunge's 10-bulb tube filled

with solution of palladious chloride and surrounded by hot water; to this bulb tube an aspirator is attached to draw a current of air through the apparatus when no more chloroform distils over.

On heating the flask, the chloroform and water vapour condense in the Woulf's bottle and the chloroform is separated mechanically and weighed. The little which remains dissolved in the water is afterwards estimated by one of the well-known methods, for instance, by means of Fehling's solution, by potassium permanganate, or by iodine. The carbon monoxide, after being freed from volatile impurities by passing through the acid, now enters the bulb tube and causes a precipitate of metallic palladium, which is then collected, ignited and weighed. One hundred parts of palladium correspond with 26.42 parts of carbon monoxide or 156.02 of chloral hydrate or 112.6 parts of chloroform.

L. DE K.

Acidity of Milk. By A. L. TOURCHOT (*Expt. Stat. Record*, 1900, 11, 578; from *Brit. Food Jour.*, 1899, 1, 199).—Determinations of acidity in a large number of milk samples showed that fairly constant results are obtained with milk less than 12 hours old, the amount of *N*/10 soda required to neutralise 10 c.c. of milk being 1.4–1.6 c.c. Greater acidity indicates that the milk is contaminated or less fresh, or else that it was from cows which had recently calved. Up to two weeks after calving, cows yield milk which may require as much as 1.8 c.c. of *N*/10 soda to neutralise 10 c.c.

When the amount of soda required exceeds 1.7 c.c. in summer, or 1.6 c.c. when the cows are stall-fed, the milk should be rejected as unfit for food. On the other hand, acidity represented by less than 1.2 or 1.4 c.c. of *N*/10 soda, in winter and in summer respectively, indicates addition of water or the presence of an unhealthy cow in the herd.

N. H. J. M.

Examination of Brown and Taylor's Official Method of Identifying Butter. By JOHN A. HUMMEL (*J. Amer. Chem. Soc.*, 1900, 22, 327–329).—In the manufacture of renovated butter, the butter-fat is melted and then rapidly cooled in a stream of cold water; this induces a semi-crystallisation of the fat, which may be recognised by the microscope. A small piece of the sample is placed on a glass slide and pressed into a thin film with a cover glass; it is then at once examined with a polarising microscope magnifying 120–150 diameters. A selenite plate is placed between the slide and the lower Nicol's prism. In every case normal butters gave a uniform blue coloured field showing the entire absence of crystals, but the renovated samples gave a blue field mottled with yellow, which varied in intensity, but was very distinct in each case.

L. DE K.

Maize Oil. By ROWLAND WILLIAMS (*Analyst*, 1900, 25, 146–147).—A table is given containing the sp. gr., potash-absorption, free fatty (oleic) acids, bromine thermal value, iodine values according to Hübl (15 hours) and to Wijs (15 minutes), and unsaponifiable matters of 8 samples of maize oil. On the whole, the figures are fairly constant, particularly those of the potash absorption and the bromine thermal value.

Notwithstanding its high iodine value (120·85—127·27), it possesses but little drying power and is not likely to take the place of linseed and similar oils in the manufacture of paints and varnishes.

L. DE K.

Nature of Klunge's Aloin Reactions, and the Oxidising Action of Cupric Salts in the Presence of Cyanogen Compounds. By EDUARD SCHAEER (*Arch. Pharm.*, 1900, 238, 42—48).—It is pointed out that a close analogy exists between Klunge's reactions for aloin and those of the author for guaiacum; the same substances (haloid salts, hydrocyanic acid, ferrocyanides, thiocyanates, and nitroprussides) which produce a blue coloration when added to a mixture of barbaloin and copper sulphate in dilute solution also produce the amethyst to cherry-red coloration when added to guaiacum-resin (guiaconic acid) and copper sulphate. In both cases, the coloration is due to an oxidation of the colouring matter; it is removed by various reducing agents. (See also this vol., i, 512).

C. F. B.

Estimation of Santonin. By JULIUS KATZ (*Archiv Pharm.*, 1900, 238, 100—102. Compare Abstr., 1899, ii, 619; this vol., ii, 122).—A controversy with Thäter on the estimation of santonin in *Flores cinæ*. Whilst, doubtless, Thäter's improved process yields a fairly pure santonin, yet it is absolutely useless for quantitative purposes, as loss of 23—56 per cent. of the total amount of santonin is caused by it.

L. DE K.

Volumetric Estimation of Alkaloids. By OTTO LINDE (*Arch. Pharm.*, 1900, 238, 102—135. Compare Abstr., 1899, ii, 534, 826).—When titrating alkaloids with standard acid and alkali, it is advisable to avoid an excess of the indicator, to have the solution as concentrated as possible, and to work at the ordinary temperature.

The following indicators may be used; they are classed according to their sensitiveness: Iodeosin, in water covered with ether; fluorescein and gallein, in water, covered with ether or in alcohol; luteol, in water or alcohol (ether or chloroform to be avoided); phenacetolin, in alcohol or water; lacmoid, in alcohol, less satisfactory in water with or without addition of ether; cochineal, in water or alcohol; tincture of brazilwood, tincture of logwood, hæmatoxylin, brazilin, azolitmin, and litmus, in water; phenolphthalein, in water (ether and chloroform to be avoided); rosolic acid, in water (ether and chloroform to be avoided); Congo-red (ether to be avoided); methyl-orange, in water; dimethyl-aminoazobenzene, in water (ether, alcohol, and light petroleum to be avoided); tropæolin, in water; tincture of turmeric and Poirrier's blue are useless.

L. DE K.

Estimation of Alkaloids by Means of a Titrated Solution of Iodine. By CARL KIPPENBERGER (*Arch. Pharm.*, 1900, 238, 135—148. Compare Abstr., 1895, ii, 467; 1896, ii, 282, 682).—A lengthy reply to Scholtz's criticism (Abstr., 1899, ii, 390). The author, although aware that the iodine process for the estimation of alkaloids does not belong to the more accurate analytical methods, still recommends it for practical purposes. Besides repeating previous experiments, fresh ones have been made with caffeine and aconitine; a solution of silver

iodide in potassium iodide is recommended as a catalytic liquid to promote the action of the iodine.

L. DE K.

[Estimation of Berberine.] By JULIUS TROEGER and OTTO LINDE (*Arch. Pharm.*, 1900, 238, 4—8).—See this vol., i, 515.

Gluten Constituents of Wheat and Flour, and their Relation to Bread-making Qualities. By H. A. GUESS (*J. Amer. Chem. Soc.*, 1900, 22, 263—268).—The following method of analysis is proposed :—
(a) Five grams of the finely-ground meal or flour are put into a 250 c.c. flask, and a 1 per cent. solution of salt is added from a pipette with sufficient pressure to prevent any tendency to clot; the flask is then filled to the mark, shaken at intervals for an hour, and left at rest for 2 hours. Of the clear filtrate, two duplicate portions of 100 c.c. are withdrawn, the proteids are precipitated with a few c.c. of a 10 per cent. solution of phosphotungstic acid, 50 c.c. of the clear filtrate evaporated with sulphuric acid, and the amide-nitrogen estimated in the usual manner.

(b) One gram of the sample is put into a 500 c.c. Kjeldahl flask, mixed with alcohol of sp. gr. 0.90, thoroughly shaken, placed in a water-bath maintained at a temperature slightly below the boiling point of the alcoholic mixture, and agitated every 10 minutes for an hour. After settling for an hour, the liquid is poured as far as practicable into a similar flask, taking care not to disturb the deposit; this is then treated four times in succession with 25 c.c. of hot alcohol to complete the extraction. The alcohol is distilled off, the nitrogen in the residue estimated, the amide-nitrogen subtracted, and the balance calculated to gliadin, using the factor $\times 5.7$.

(c) The residue from the alcohol extraction, when cold, is treated with 250 c.c. of a 1 per cent. solution of salt, and allowed to settle for an hour; after pouring off the liquid through a filter, the mass is again treated with another 250 c.c. of salt solution, shaken at intervals for an hour, and allowed to settle for 2 hours, when the liquid is decanted through the same filter. The filter and contents are added to the residue in the flask, and the nitrogen estimated and calculated to glutenin.

The results of the analyses of 104 samples are communicated in a table. At present, it cannot be said that there seems to be a true relation between the ratios of the various proteids and the practical value of the sample for bread making, but there is no doubt a direct and very intimate connection between them.

L. DE K.

General and Physical Chemistry.

Origin of Certain Unknown Lines in the Spectra of Stars of the β -Crucis Type, and the Spectrum of Silicon. By JOSEPH LUNT (*Proc. Roy. Soc.*, 1900, **66**, 44—50).—The three unknown lines present in the spectra of β -Crucis, ϵ -Canis Majoris, and stars of that type (Gill, *Abstr.*, 1899, ii, 718), have been obtained from pure helium and argon tubes with a highly disruptive spark, and are shown to be due to silicon. In the silicon spectrum from these tubes, the enhanced lines noted by Lockyer are less prominent than in the spectrum obtained from silicon tetrafluoride with an intensely disruptive spark; it therefore seems that great variations in the relative intensities of the silicon lines occur in stellar spectra. This behaviour of the silicon lines is important in the determination of relative stellar temperatures (compare Lockyer, this vol., ii, 181). J. C. P.

Liquid Absorption Spectra in the Ultra-Red. By L. PUCCIANI (*Nuovo Cimento*, 1900, [iv], 11, 241—278).—The absorption spectra of the following liquids in the ultra-red have been determined for wave-lengths of 2.75μ and less: Benzene, toluene, *o*-, *m*-, and *p*-xylene, ethylbenzene, methyl iodide, ethyl iodide, ether, alcohol, methyl alcohol, pyridine, allyl alcohol, carbon disulphide, and carbon tetrachloride. The results, together with those of Donath (*Ann. Phys. Chem.*, 1896, [ii], **58**, 609), on oil of turpentine, oil of juniper, oil of rosemary, oil of lavender, safflower oil, oil of olives, and petroleum show that liquid compounds whose molecules contain carbon combined directly with hydrogen exhibit a maximum of absorption for the wave-length 1.71μ . Further, besides this maximum, all the benzene compounds examined, and also pyridine, have two other maxima of absorption in common, these being probably due to the peculiar structure of their molecules. The spectra of the three alcohols are very similar, and have maxima of absorption for a wave-length of about 2.10μ . The three isomeric xylenes show absorptions almost, although not quite, identical. At about 2.32μ , another maximum occurs for toluene, *o*-, *m*-, and *p*-xylene, ethylbenzene, ethyl iodide, ether, and methyl and ethyl alcohols. T. H. P.

Sensitiveness of Silver and of some other Metals to Light. By JAMES WATERHOUSE (*Proc. Roy. Soc.*, 1900, **66**, 490—504).—The author confirms Moser's observation that silver, exposed under ordinary conditions, is distinctly sensitive to light; not only can an invisible, developable image be obtained, but by prolonged exposure printed-out impressions are produced which are clearly visible after exposure. Blue and violet rays are shown to be most active in producing this effect. It seems that heat does not play any active part in the production of the images, although higher temperatures may accelerate the action of light. When a pure silver plate has been raised to a red heat, plunged in dilute sulphuric acid, washed,

dried, and exposed, no image is produced. Of other metals, the only one that is similarly sensitive is lead. J. C. P.

Artificial Radio-active Barium. By A. DEBIERNE (*Compt. rend.*, 1900, 131, 333—335).—When a highly radio-active salt of actinium is added to a barium chloride solution, the latter becomes radio-active, and the results are more marked if the barium is precipitated as sulphate and reconverted into chloride, the actinium being separated by means of ammonium hydroxide. The radio-activity of the barium increases with the duration of its contact with the actinium salt, and may become several hundred times as great as that of uranium. The radiation thus induced in the barium resembles that of the radio-active barium obtained from pitchblende, is associated with the atoms of the metal, and persists through various chemical changes; it ionises gases, excites the phosphorescence of barium platinocyanide, and acts on photographic plates. Part of the radiation is deflected in a magnetic field, and the anhydrous chloride of the metal is self-luminous. Further, the barium chloride made radio-active by induction can be fractionated, and the radio-activity is more intense in the first crystals. On the other hand, the salts do not show the spectrum of radium, and the induced radio-activity gradually diminishes in intensity (compare this vol., ii, 351, 352, 480). C. H. B.

Spectrum of Radium. By EUGÈNE DEMARCAY (*Compt. rend.*, 1900, 131, 258—259).—A specimen of radium chloride, prepared by Mme. Curie, and dissolved in hydrochloric acid, gave a spark spectrum in which the barium lines were feeble, and only the line 4554·4 had any marked intensity. On the other hand, it gave a brilliant radium spectrum, which did not contain any lines in addition to those already observed (this vol., ii, 83). Two bands described (*loc. cit.*) as faint and nebulous were, however, very distinct, with maximum intensity at about 4627·5 and 4455—4453·4 respectively. The line 4364·2, formerly attributed to radium, seems to be identical with the platinum line 4364·4, and the origin of the very feeble line 4600·3 is uncertain. In general character, the radium spectrum resembles the spectra of the alkaline-earth metals. The low intensity of the barium spectrum indicates that this specimen of radium chloride is practically pure.

C. H. B.

Radio-activity of Uranium. By SIR WILLIAM CROOKES (*Proc. Roy. Soc.*, 1900, 66, 409—423).—In agreement with an observation of M. and Mme. Curie (this vol., ii, 82), the author finds that all radio-active minerals contain either uranium or thorium; pitchblende shows the most intense action, and gives an effect roughly proportional to the percentage of uranium it contains. In the preparation of pure uranium nitrate, it was observed (1) that solution of the nitrate in ether and subsequent crystallisation gave an inactive product; (2) that the active constituent was concentrated in the aqueous layer formed when crystallised uranium nitrate and ether are shaken up together. The portion insoluble in ether, when evaporated to dryness with nitric acid and crystallised from water, has the same appearance (1) as ordinary uranium nitrate, (2) as the product from the ethereal solution, evapo-

rated to dryness and crystallised from water. When the uranium nitrate from the portion insoluble in ether is submitted to fractional crystallisation, the radio-active substance is concentrated in the mother liquor. A highly active uranium nitrate obtained in this way was dissolved in water, and excess of ammonia added; the whole of the radio-activity was found to reside in the ammonium uranate formed. Another portion of active uranium nitrate was dissolved in water, and excess of ammonium carbonate added; the first formed precipitate almost entirely redissolved, but a light brown, fluorescent portion, remaining insoluble in excess, was found to contain almost the whole of the radio-active constituent. For this the author uses provisionally the symbol UrX , and shows that its action differs from that of polonium, inasmuch as the emanations from the latter cannot pass through glass, aluminium, or lead. UrX is further distinguished from polonium by its non-volatility and its chemical behaviour. It is not so easy to settle whether UrX is distinct from radium, although many considerations point to its not being this substance; thus radium sulphate is said to be insoluble in water and acids, whilst UrX dissolves easily to a clear solution in dilute sulphuric acid.

Similar experiments with thorium nitrate point to the possibility of separating a radio-active substance from thorium. J. C. P.

Behaviour of Radium at Low Temperatures. By O. BEHRENDSEN (*Ann. Phys.*, 1900, [iv], 2, 335—337).—The power of certain substances possessing radio-activity to discharge a metallic conductor has been previously shown (*Ann. Phys. Chem.*, 1896, [ii], 69, 220) to be diminished by lowering the temperature. The same behaviour has now been observed in the case of a radium preparation. J. C. P.

Velocity of the Ions produced in Gases by Röntgen Rays. By JOHN ZELENY (*Proc. Roy. Soc.*, 1900, 66, 238—241).—The author has determined the velocities of the ions produced in air, oxygen, carbon dioxide, and hydrogen by Röntgen rays. Moisture generally diminishes the ionic velocity, this effect being specially marked in the case of negative ions. Except for moist carbon dioxide, the velocity of the negative ion is greater than that of the positive ion (compare Rutherford, *Abstr.*, 1898, ii, 112; Townsend, *Abstr.*, 1899, ii, 729). J. C. P.

Electrical Conductivity in Gases traversed by Cathode Rays. By J. C. McLENNAN (*Proc. Roy. Soc.*, 1900, 66, 375—378).—It has been shown that when a gas is traversed by Röntgen or uranium rays, positive and negative ions are produced; the author finds that this occurs also under the influence of cathode rays. When cathode rays of a given strength pass through a gas, the number of ions produced per second in 1 cub. cm. depends only on the density of the gas, and is independent of its chemical composition. Under rays of constant intensity, the ionisation in a particular gas varies directly as the pressure. It is shown that the values of relative ionisation in different gases by Röntgen rays of constant intensity agree well in most cases with those obtained for cathode rays. J. C. P.

Electrical Effects due to Evaporation of Sodium in Air and other Gases. By W. CRAIG HENDERSON (*Proc. Roy. Soc.*, 1900, **66**, 183—186).—When sodium is fused and boiled in an iron cylinder, an electrometer connected (1) with the cylinder, (2) with a copper plate suspended in the vapour, shows considerable electrification; this, however, is not observed when the air in the cylinder is replaced by coal gas, so that the electrification is due to oxidation, and not merely to evaporation. J. C. P.

Electrolytic Reduction of Difficultly Reducible Substances in Sulphuric Acid Solution. By JULIUS TAFEL (*Zeit. physikal. Chem.*, 1900, **34**, 187—228; also *Ber.*, 1900, **33**, 2209—2224).—By comparing the volumes of hydrogen liberated (1) in a sulphuric acid voltameter, (2) at the cathode of a cell containing a reducible substance in sulphuric acid solution, it is possible to follow the course of the reduction. With an apparatus constructed on this principle, the author has determined under what conditions the process of reduction is a regular one. In the case of caffeine, the reducible substance mainly used in the experiments, no reduction takes place except when the cathode is of lead or mercury, the cathode potential of these metals being specially high. The addition of small quantities of other metals to the cathode liquid stops the reduction process, and there is a simultaneous fall in the cathode potential. In certain cases, the foreign metal is rendered harmless, and the reduction process started again by the addition of lead acetate. In view of these experiments, it is probable that the irregularities usually observed in the reduction process are due to small quantities of foreign metals. To obtain consistent results, it is further necessary that the lead electrodes should be prepared electrolytically, and have a superficial coating of finely divided peroxide. Rise of temperature accelerates the reduction of caffeine, but only to a small extent (compare Abstr., 1899, i, 268).

J. C. P.

Chromium Cell for the Rectification of Alternating Currents. By J. LIVINGSTON R. MORGAN and W. A. DUFF (*J. Amer. Chem. Soc.*, 1900, **22**, 331—334).—Two electrodes, one of chromium and the other of platinum, are immersed in dilute sulphuric acid. When the platinum is made the anode, the current passes freely; but if the chromium is made the anode, no current goes through the cell. By using the chromium as anode and very gradually increasing the impressed E.M.F., it is possible to stop any current entirely until a pressure of about 75 volts is reached. When the increase in the E.M.F. is made so rapidly that the current passes from chromium to platinum, or after the cell breaks down by the application of more than 75 volts, a peculiar result is obtained. Unlike the aluminium cell, the chromium cell, after it has broken down, is still an asymmetrical resistance, but only when the platinum plate is made the anode. With chromium as the anode, the current now passes freely. If in this condition the cell is broken down by the application of too high an E.M.F. to the platinum anode, another reversal takes place, so that about 75 volts can again be stopped, using the chromium as anode. This change in the behav-

four of chromium is doubtless due to the change from the 'active' to the 'inactive' state (Hittorf, *Abstr.*, 1898, ii, 363; 1900, ii, 127).

The authors consider that these results confirm the theory that the action of the aluminium cell is due to the formation of a resistant film, as suggested by Norden (this vol., ii, 404; compare also Wilson, *Abstr.*, 1899, ii, 540). E. G.

Existence of Thermal Centres of Stability in Compounds. By GEOFFREY MARTIN (*Chem. News*, 1900, 81, 301—304).—The heat of formation of a compound varies with the temperature, and the kinetic theory leads to the conclusion that for an exothermic compound the heat of formation diminishes as the temperature rises. Victor Meyer has shown that the heat of formation of hydrogen iodide is at first negative, becomes zero at 324°, and at higher temperatures is positive; an example of an endothermic compound changing into an exothermic one. The author supposes that this is a general phenomenon, and that the exothermic compound may pass back again to the endothermic stage as the temperature rises. According to this view, the positive or negative value of the heat of formation is a periodic function of the temperature. Each temperature at which the heat of formation is zero would be a centre of stability. It is not to be expected that a gaseous substance would exist at all points on this curve, but it should exist at least at the centres of stability. The author discusses evidence in favour of this, and points out, *inter alia*, that silicon hexachloride, which at 800° is completely dissociated into tetrachloride and silicon, exhibits no dissociation if suddenly raised above 1000°. This compound, therefore, is stable above 1000° and below 350°, but cannot exist undissociated at intermediate temperatures. The maximum of conductivity shown by certain acids in solution is regarded as an analogous phenomenon. J. C. P.

Weight of Hydrogen Desiccated by Liquid Air. By LORD RAYLEIGH (*Proc. Roy. Soc.*, 1900, 66, 334).—The density of hydrogen dried by liquid air, acting as a cooling agent, is the same as that obtained when phosphoric oxide is used to effect desiccation. J. C. P.

Distillation of Liquid Air, and the Composition of the Gaseous and Liquid Phases. I. At Constant Pressure By EDWARD C. C. BALY (*Phil. Mag.*, 1900, [v], 49, 517—529).—The experiments were made in order to render possible the determination of the temperature of boiling air by the analysis of the gas evolved. The results are summed up in two curves which show (1) the boiling point at 760 mm. of all mixtures of oxygen and nitrogen, (2) the temperature at which any mixture of oxygen and nitrogen will liquefy, and the composition of the liquid formed. When $r'/100$ is the ratio of the compounds in the gaseous phase, and $r/100$ the corresponding ratio in the liquid phase, then the most probable relation between r and r' throughout the distillation is found to be $r' = 0.2097 \times r^{1.06737}$ (compare Lehfeldt, *Phil. Mag.*, 1895, [v], 40, 397). There does not appear to be any connection between the ratio of the vapour pressures and the composition of the gaseous phase in the distillation of oxygen and nitrogen at constant pressure. J. C. P.

Viscosity of Argon as affected by Temperature. By LORD RAYLEIGH (*Proc. Roy. Soc.*, 1900, **66**, 68—74).—The time of passage of a quantity of argon through a capillary tube has been determined at two different temperatures. It was thought probable that the viscosity of argon would vary with the temperature in another manner than that of the diatomic gases, oxygen, hydrogen, and nitrogen, but the experimental work shows that there is no great difference. When $\mu'/\mu = [\theta'/\theta]^n$, where μ' and μ are the viscosities at the absolute temperatures θ' and θ , then n has the following values: air (dry), 0.754; oxygen, 0.782; hydrogen, 0.681; argon (impure), 0.801; argon (best), 0.815. J. C. P.

Influence of the Medium on the Velocity of Reaction. By GUSTAV BUCHBÖCK (*Zeit. physikal. Chem.*, 1900, **34**, 229—247).—A previous investigation (Abstr., 1897, ii, 398) has shown that the velocity of decomposition of carbonyl sulphide in various aqueous solutions depends partly on the viscosity of the solutions. This investigation has now been amplified on the basis of van't Hoff's theory, according to which the velocity of reaction in various media is defined by the equation $dC/dt = \kappa C/S$; here C is the concentration, and S represents the quantities of the reacting substance (carbonyl sulphide) which are in equilibrium with each other in the various media. The author has taken isosmotic solutions of a number of salts and acids, and determined the absorption coefficient and decomposition velocity constant of carbonyl sulphide in these solutions; he has further measured the viscosity of the solutions. In general it is seen that the greater the viscosity the smaller the value of κ . The product of the two has for inorganic solutions a fairly constant value (8.84), quite different, however, from the value obtained in the case of the organic acids. It is pointed out that the product of reaction velocity and viscosity is a linear function of the absolute quantity of water in the solutions; if allowance is made for this, it is seen that the velocity of decomposition of thiocarbonic acid in such aqueous isosmotic solutions as are in equilibrium with respect to thiocarbonic acid, is inversely proportional to the viscosity of the solutions. J. C. P.

Reply to Criticism. [Chemical Affinity.] By WILHELM VAUBEL (*Chem. Zeit.*, 1900, **24**, 371—373).—A recapitulation of the author's theories (see this vol., ii, 264, 274), and a reply to Küster's criticisms in particular. J. C. P.

Affinity Constants of Acids containing a Ring of Seven Carbon Atoms. By W. A. ROTH (*Ber.*, 1900, **33**, 2032—2035. Compare Willstätter, Abstr., 1899, i, 651).—The following affinity constants in absolute units at 25° have been determined: α -Cycloheptatrienecarboxylic acid (α -isophenylacetic acid), $K = 0.003672$; β -cycloheptatrienecarboxylic acid (β -isophenylacetic acid), $K = 0.004101$; Δ^1 -cycloheptenecarboxylic acid, $K = 0.000992$ and for another solution, after correcting for the conductivity of the water, $K = 0.000928$. Δ^2 -Cycloheptenecarboxylic acid gave, in three different solutions, the corrected values $K = 0.00267$, 0.00260 and 0.002606 respectively; this acid appears to undergo a gradual chemical change resulting in a

diminution of the value of K , the highest number for which is hence probably the most accurate. T. H. P.

Nature and Properties of Colloidal Solutions. By GIUSEPPE BRUNI and N. PAPPADÀ (*Atti Real. Accad. Lincei*, 1900, [v], 9, i, 354—358).—Solutions of the following colloids—silicic acid, ferric hydroxide, chromic hydroxide, ferric ferrocyanide, egg albumin, and gelatin—were prepared and submitted to dialysis for varying periods, never less than a fortnight, the external liquid being frequently changed. In no case was any of the colloid found to diffuse through the dialyser, and further, the freezing points of the colloidal solution and of the external liquid with which it is in equilibrium show only very small differences, which are in both senses and within the limits of experimental error. Vapour tension experiments, carried out by a modification of Ostwald and Walker's method, a current of air being passed through a series of five flasks, the first three containing the colloidal solution, and the others the corresponding exterior liquid from the dialysing apparatus, showed no variation in the vapour pressures of the various liquids. Semi-colloids, for example, dextrin or molybdic acid, in solution pass comparatively readily through a dialyser and also give small depressions of the freezing point, which are, however, quite appreciable and proportional to the concentration; dextrin, for example, gives a molecular weight 1135, corresponding with the formula $(C_6H_{10}O_5)_7$. Semi-colloids must hence be regarded as substances which, in solution, have very high molecular weights. With colloids, however, no real solution takes place, the substance remaining suspended in the liquid in a very fine state of subdivision. This view finds confirmation in the application of the phase rule to such solutions. If they are true solutions, on freezing there would be three co-existent phases—ice, solution, and vapour—the system being mono-variant, whilst in the case of a solution containing a solid in suspension, there would be another phase and the system would be non-variant. That the latter is the fact is shown by the constancy of the temperature of freezing, which in the former case would vary with the concentration. This conclusion is in accord with that of Stoeckel and Vanino (this vol., ii, 11), arrived at from a study of the optical properties of colloidal solutions of the metals. T. H. P.

Nitrogen Peroxide as a Solvent. By GIUSEPPE BRUNI and P. BERTI (*Atti Real. Accad. Lincei*, 1900, [v], 9, i, 321—326).—The cryoscopic behaviour of solutions of the following compounds in nitrogen peroxide has been examined: nitromethane, nitroethane, acetic, butyric, trichloroacetic, picric, and nitric acids. Nitromethane, nitroethane, and picric acid show normal molecular weights, whilst all the other compounds examined show depressions of the freezing points less than the normal, hence nitrogen peroxide is not only devoid of dissociating power but must be classed with those solvents in which hydroxy-compounds are associated. T. H. P.

Cryoscopic Behaviour of Nitro-derivatives in Formic Acid. I. By GIUSEPPE BRUNI and P. BERTI (*Atti Real. Accad. Lincei*, 1900, [v], 9, i, 273—279).—The cryoscopic behaviour of the

following nitro-derivatives in formic acid has been determined: Nitrobenzene, *m*-dinitrobenzene, 1:3:5-trinitrobenzene, 2:4:6-trinitrotoluene, 1-chloro-2:4:6-trinitrobenzene, picric acid, methyl picrate, *p*-nitrobenzoyl chloride, nitromethane, nitroethane, chloropicrin. The results show that the aromatic nitro-derivatives are all more or less dissociated in formic acid solution, whilst those of the aliphatic series show no signs of dissociation. Picric acid is not more dissociated than its methyl ether, the presence of the hydroxyl group being apparently without effect on the dissociation, which, however, tends to increase with the accumulation of electro-negative groups in the molecule. The presence of a small quantity of water in the formic acid does not increase its dissociating power.

This dissociation of aromatic nitro-derivatives in formic acid solution is probably due to the formation of an additive product of the type $R \cdot NO(OH)(CO_2H)$. Such compounds would be capable of dissociation and similar additive products should also be formed with acetic acid, but in this case they are not indicated by the cryoscopic behaviour, since acetic acid has no dissociating power. One fact in favour of this hypothesis is that solutions of aromatic polynitro-derivatives in anhydrous formic acid are colourless even at high concentrations, whilst with other solvents, whether possessed of dissociating power or not, they form intensely yellow solutions.

T. H. P.

Behaviour of Nitro-derivatives in Formic Acid Solution. II. By GIUSEPPE BRUNI and P. BERTI (*Atti Real Accad. Lincei*, 1900, [v], 9, i, 393—400).—In formic acid solution, the following nitro-compounds all show abnormally small molecular weights on freezing: trinitro-*p*-xylene, *o*-, *m*-, and *p*-chloronitrobenzenes, *o*-, *m*-, and *p*-nitrobenzoic acids, methyl *o*-, *m*-, and *p*-nitrobenzoates.

The molecular weights of *s*-trinitrobenzene, 2:4:6-trinitroanisole, dinitromesitylene and trinitromesitylene were determined in boiling formic acid, the last two compounds being almost insoluble in the freezing acid. The molecular raising of the boiling point of formic acid is $\kappa = 34$, as determined for solutions of β -naphthol and benzoic acid. Of the four compounds mentioned, the first three show marked dissociation in boiling formic acid, whilst trinitromesitylene gives the normal molecular weight, whence the conclusion is drawn that for a compound to show dissociation in formic acid solution the presence of a mobile hydrogen atom in the molecule is necessary.

To test the hypothesis advanced in a former paper (see preceding abstract), according to which dissociation in formic acid is due to the formation of an additive product of the acid with the dissolved substance, the freezing point curve for mixtures of formic acid and *o*-chloronitrobenzene was studied. The curve is composed of two branches meeting in one cryohydric point, as is the case for mixtures of two substances which do not combine, and completely excludes the existence of an additive compound.

T. H. P.

Oxidations with Free Oxygen. By WILHELM OSTWALD (*Zeit. physikal. Chem.*, 1900, 34, 248—252).—The occurrence of ozone in oxidation processes has been attributed to the primary formation of a higher oxide of the oxidisable substance, which then splits up into a

lower oxide and ozone. The author deals with the theoretical side of this view, and points out that ozone has a higher oxidation potential than the oxygen from which it is derived, and that the energy necessary to raise the oxidation potential must be obtained from some other reaction, namely, the formation of a more stable oxide. These two processes, however, must be intimately connected with one another, and expressible by a single chemical equation with definite integral coefficients. Thus, when ozone occurs in the oxidation of phosphorus, it is incorrect to suppose that (1) energy is derived from the oxidation of the phosphorus, (2) this energy converts oxygen into ozone, the two processes being independent; on the contrary, they must be intimately related, and this is done by postulating the intermediate formation of a higher oxide. The criterion for the formation of such an intermediate compound is the occurrence of the final products in definite chemical proportions. J. C. P.

Crystallographic Characters of some Isomorphous Potassium Salts. By F. CORIO (*Zeit. Kryst. Min.*, 1900, 32, 524—526; from *Atti Soc. Sci. Nat. Modena*, 1898, 16, 73—117).—Optical and crystallographic determinations are given of potassium sulphate and potassium chromate and of crystals containing various proportions of these two salts. L. J. S.

Comparative Crystallographical Study of the Double Selenates of the Series $R_2M(SeO_4)_2 \cdot 6H_2O$. I. Salts in which M is Zinc. By ALFRED E. TUTTON (*Proc. Roy. Soc.*, 1900, 66, 248—250).—In the double salts examined, R represents potassium, rubidium, and caesium. The characters of the rubidium double selenate lie invariably between those of the potassium and caesium salts. Comparison of the results obtained with those previously communicated (*Trans.*, 1893, 63, 337; 1896, 69, 344), shows that the replacement of sulphur by selenium is generally accompanied by a change in the morphological and physical constants similar to that accompanying the replacement of one alkali metal by another of higher atomic weight. In the heavier selenate molecules, however, the amount of change caused by varying the alkali metal is often less than in the case of the double sulphates. J. C. P.

Acetylene Gas as Fuel in Chemical Laboratories. By ARTHUR LACHMAN (*Amer. Chem. J.*, 1900, 24, 39—45).—The author thinks that, in cost, convenience, or feasibility, acetylene cannot compete with "gasoline gas" (air saturated with gasoline vapour) as a laboratory fuel. J. J. S.

Etymological Researches on the Names of the Chemical Elements, from which the International and National Symbols are derived, with Special Reference to the German Names. By PAUL DIERGART (*J. pr. Chem.*, 1900, [ii], 61, 497—531).—An etymological paper, which traces the derivation of the common names of the elements and throws much light on their history. R. H. P.

Inorganic Chemistry.

Electrolysis of Concentrated Hypochlorite Solutions. By ANDRÉ BROCHET (*Compt. rend.*, 1900, 131, 340—343).—When a solution of sodium hypochlorite containing sodium hydroxide is electrolysed, the proportion of hypochlorite at first diminishes rapidly, and afterwards more slowly, finally becoming constant. At the same time, the proportion of chlorate increases, at first very rapidly, then more slowly, and afterwards at a constant rate. The reduction at the cathode is almost constant for some time, then diminishes somewhat rapidly, and afterwards becomes constant again; the oxidation at the anode is at first constant, then increases slowly, and finally reaches a limit. The presence of sodium hydroxide does not affect the reduction of the hypochlorite, but very materially affects the limits of the reactions.
C. H. B.

Composition of Nitrogen Iodide. By F. D. CHATTAWAY (*Amer. Chem. J.*, 1900, 24, 138—158).—See Proc., 1899, 15, 18.

Action of Light on Nitrogen Iodide. By F. D. CHATTAWAY and K. J. P. ORTON (*Amer. Chem. J.*, 1900, 24, 159—167).—See Proc., 1899, 15, 18.

Transformation of Hyponitrous Acid into Hydrazine. By FREIHERR VON BRACKEL (*Ber.*, 1900, 33, 2115—2116).—An acid aqueous solution of hyponitrous acid was treated with sodium hydrogen sulphite in the cold; the product reduced Fehling's solution in the cold. It was concentrated under diminished pressure and reduced with zinc dust and acetic acid; the solution, when freed from zinc, reduced Fehling's solution in the cold, and gave a precipitate of benzalazine with benzaldehyde; it must therefore have contained hydrazine.
C. F. B.

Nitrohydroxylaminic Acid. By ANGELO ANGELI and FRANCESCO ANGELICO (*Gazzetta*, 1900, 30, i, 593—595).—The *potassium*, $K_2N_2O_3$, *calcium* (with $\frac{1}{2}H_2O$), *strontium* (with H_2O), *lead*, and *cerium*, $Ce_2(N_2O_3)_3 \cdot Ce(OH)_3$, salts of nitrohydroxylaminic acid have been prepared. Solutions of the sodium salt rapidly absorb oxygen from the air, forming sodium nitrite, which in presence of excess of the nitrohydroxylamate partially undergoes further oxidation to nitrate. Nitrohydroxylaminic acid, which is unstable and could not be isolated, decomposes in various ways depending on the conditions; by means of acids it is broken up almost quantitatively according to the equation: $H_2N_2O_3 = 2NO + H_2O$, small quantities of nitrous and possibly of hyponitrous acid also being formed. On boiling the sodium salt with water, one half of the total nitrogen is evolved in the form of nitrous oxide and the rest remains as sodium nitrite, $2H_2N_2O_3 = 2HNO_2 + N_2O + H_2O$; this reaction indicates the structure $O:N(OH):N \cdot OH$.

for the acid. On heating the sodium salt to incipient fusion, sodium nitrite and hyponitrite are formed thus: $2\text{O}\cdot\text{N}(\text{OH})\cdot\text{N}\cdot\text{OH} = 2\text{HNO}_2 + \text{OH}\cdot\text{N}\cdot\text{N}\cdot\text{OH}$. The aqueous solution of the sodium salt readily reacts with aldehydes with development of heat; with acetaldehyde, the sodium salts of nitrous and acetohydroxamic acids are formed. T. H. P.

Solubility of Quartz in Sodium Silicate Solutions. By GIORGIO SPEZIA (*Atti Accad. Sci. Torino*, 1900, 35, 750—761).—Dilute solutions of sodium silicate acting on quartz at high temperatures exert a decided solvent action on it. At lower temperatures, the quartz is re-deposited, Sterry Hunt's hypothesis that such deposition is due mainly to diminution in pressure being in this case untenable. T. H. P.

Constitution of Glass and Allied Products. By KARL ZULKOWSKI (*Chem. Centr.*, i, 1041—1042; from *Chem. Ind.*, 1900, 23, 108—114).—Like silicic acid, boric acid forms higher poly-acids of the type $\text{B}_{2n}\text{O}_{3n-1}(\text{OH})_2$ or $n\text{B}_2\text{O}_3, \text{H}_2\text{O}$. When melted with alkali carbonates, it behaves like silicic acid, and with excess of the carbonate tends to form a metaborate, hence in boron glass probably only polymetaborates are present. Compounds of borosilicic acid probably occur in silicate glass containing boric acid.

When silicate glass is rendered opaque by adding tin dioxide, polymetastannates which are less fusible and are insoluble in the fused mass are formed. The opaque particles of enamel glass probably also consist of these compounds. Whilst, however, polymetastannates of the type $\text{KO}\cdot\text{SnO}\cdot\text{O}\cdot\text{SnO}\cdot\text{OK}$ are formed by fusing tin dioxide with potassium carbonate, the ordinary metastannate, $\text{SnO}(\text{ONa})_2$ is obtained with sodium carbonate; the production of normal or acid stannates seems to be less dependent on the kind of alkali than on the melting point.

Unlike the anhydrides of the other glass-forming acids, calcium metaphosphate, when melted with potassium carbonate, forms an orthophosphate. The composition of pure phosphate glass corresponds with that of silicate glass, and the polymetaphosphoric acids formed are of the type $\text{P}_{2n}\text{O}_{5n-1}(\text{OH})_2$ or $n\text{P}_2\text{O}_5, \text{H}_2\text{O}$. Calcium metaphosphate is prepared by gradually heating and then melting crystallised monocalcium orthophosphate at an orange-red heat. E. W. W.

So-called Electrolytic Silver Peroxide [Silver Peroxynitrate. By OTTO KAR SÜLC (*Zeit. anorg. Chem.*, 1900, 24, 305—313. Compare Abstr., 1896, ii, 521).—The compound $\text{Ag}_7\text{NO}_{11}$, obtained by the electrolysis of a solution of silver nitrate, has been subjected to further investigation. When dissolved in ammonia, it liberates 2·8 per cent. of nitrogen, that is, 2 mols. of ammonia are oxidised by 3 of the oxygen atoms of the peroxide. When heated at 120° during 16 hours, it decomposes, evolving 8·46 per cent., or 5 atomic proportions of oxygen, whilst at lower temperatures the decomposition is slower, and does not proceed so far. From these results, the author proposes the formula $\text{AgNO}_3, 3\text{Ag}_2\text{O}_2, 2\text{O}$ for the substance (compare Mulder and Heringa, *loc. cit.*). E. C. R.

Manganese Compounds. I. Ammonium Permanganate. By ODIN T. CHRISTENSEN (*Zeit. anorg. Chem.*, 1900, 24, 203—219).—Ammonium permanganate can be prepared by the action of ammonium chloride on potassium permanganate solution at 70—80°, or on finely-powdered silver permanganate, and purified by recrystallisation from water at 70°. When left in a closed vessel at the ordinary summer temperature, it is completely decomposed with the formation of ammonium nitrate and the insoluble manganese oxide, $22\text{MnO}_2, \text{MnO}, x\text{H}_2\text{O}$, crystallised in pseudomorphs of ammonium permanganate. At higher temperatures (42—50°), a similar decomposition takes place in a few days, whilst at 58° the salt decomposes in a few hours with explosive violence. The same compounds are obtained, together with a small quantity of nitrogen, on boiling the substance with water, whilst when it is heated with ammonia, the decomposition products are nitrogen, ammonium nitrite, a small quantity of ammonium nitrate, and a hydrated manganese oxide, which, after drying, contains 85·31 per cent. of manganous oxide and 14·69 per cent. of active oxygen. When heated with nitric acid, the hydrated manganese oxide $22\text{MnO}_2, \text{MnO}, 28\text{H}_2\text{O}$ is formed, containing, however, a small quantity of ammonia which cannot be eliminated. E. C. R.

Ferrous Iodide. By C. LORING JACKSON and I. H. DERBY (*Amer. Chem. J.*, 1900, 24, 15—31).—Ferrous iodide was prepared by heating clean iron wire clippings in an atmosphere of nitrogen saturated with iodine vapour. The product forms deep red plates with a slightly brownish tinge, but in thicker masses is nearly black; it is extremely deliquescent, decomposes at a moderate heat in the presence of oxygen, and when exposed in a desiccator it turns white, but then gradually evolves iodine and becomes grey or black. The white compound is probably a hydrate, $\text{FeI}_2 \cdot 2\text{H}_2\text{O}$. Carius and Wanklyn's (*Annalen*, 1861, 120, 69) and Thomson's (*Compt. rend.*, 1862, 55, 615) methods for the preparation of ferrous iodide have also been tried, and the product obtained in each case had the appearance just described.

Anhydrous ferrous iodide readily absorbs ammonia gas, yielding a voluminous, white, amorphous powder of the composition $\text{FeI}_2 \cdot 6\text{NH}_3$, which is readily decomposed by water, and, when treated with bromine vapour, yields ferric bromide, ammonium bromide, and *ammonium bromoiodobromide*, NH_4BrIBr . This compound, which may also be obtained by the action of an ethereal solution of iodine bromide on ammonium bromide, is a lustrous green substance, dissolves in ether, and readily decomposes when exposed to the air, leaving a residue of ammonium bromide. J. J. S.

Action of Potassium Persulphate on Cobalt Salts. By F. MAWROW (*Zeit. anorg. Chem.*, 1900, 24, 263—268).—A solution of cobalt sulphate or nitrate, when warmed with excess of potassium persulphate, yields a dark brown precipitate containing $\text{Co}_3\text{O}_4, 3\text{H}_2\text{O}$ mixed with sulphates. The oxide $\text{Co}_3\text{O}_4, 3\text{H}_2\text{O}$ is obtained by warming cobaltous hydroxide with excess of potassium persulphate, and, after washing with water, heating the product at 100° with dilute nitric acid. The yield amounts to one-third of the cobaltous hydroxide.

The oxide $\text{Co}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$, obtained by treating cobaltous hydroxide with excess of potassium persulphate in the presence of excess of potassium hydroxide solution of sp. gr. 1.18—1.3, is a black precipitate which oxidises oxalic acid to carbon dioxide when heated with it, and is insoluble in cold, and only partially soluble in hot, concentrated nitric acid. E. C. R.

Preparation of the Blue Oxide of Molybdenum and of Metallic Molybdenum. By ALLEN ROGERS and F. H. MITCHELL (*J. Amer. Chem. Soc.*, 1900, 22, 350—351).—The blue oxide of molybdenum is obtained by the addition of stannous chloride to a solution of ammonium molybdate slightly acidified with nitric acid. The precipitate is washed as quickly as possible, drained, and dried at 100° ; it seems to have the composition Mo_3O_8 , and is more readily reduced than the trioxide when heated in a current of hydrogen. Small quantities may be quickly reduced by placing the substance in a cavity in the lower of two carbon poles, and passing the electric current in an atmosphere of hydrogen; the resulting molybdenum is a very hard, dull steel-grey mass. E. G.

Double Nitrates of Quadrivalent Cerium and of Thorium. By RICHARD JOS. MEYER and RICHARD JACOBY (*Ber.*, 1900, 33, 2135—2140).—Basic ceric nitrate, $\text{Ce}(\text{NO}_3)_3 \cdot \text{OH}$, has been obtained crystalline. Double nitrates of quadrivalent cerium and of thorium have been prepared (not all for the first time) of the types $\text{M}'_2\text{M}^{\text{IV}}(\text{NO}_3)_6$ and $\text{M}''\text{M}^{\text{IV}}(\text{NO}_3)_6 \cdot 8\text{H}_2\text{O}$, where $\text{M}^{\text{IV}} = \text{Ce}$ or Th , $\text{M}' = \text{NH}_4$, Rb or Cs , and $\text{M}'' = \text{Mg}$, Zn , Ni , Co , and Mn (and also Sr , when $\text{M}^{\text{IV}} = \text{Th}$). In addition, a salt, $\text{NH}_4\text{Th}(\text{NO}_3)_5 \cdot 5\text{H}_2\text{O}$, belonging to a different type, was prepared. Details are to be published later. C. F. B.

[Purification of] Commercial Thorium Nitrate. By WILHELM MUTHMANN and E. BAUR (*Ber.*, 1900, 33, 2028—2031).—To purify thorium nitrate, 840 grams of the commercial product were dissolved in 5 litres of water, and into the solution was passed steam under 3 atmospheres pressure while 1 litre of 6 per cent. potassium chromate solution was added in drops. By repeating this operation six times, crystalline thorium chromate, $\text{Th}(\text{CrO}_4)_2 \cdot 3\text{H}_2\text{O}$, was obtained which yielded 320 grams of the white oxide, containing impurities to the extent of about 0.3 per cent. Mantles for incandescent burners prepared from this purified oxide give a light 1.3—1.4 times as intense as those prepared from the impure thorium salt. Impurities in the small proportion (1 per cent.) of ceria used in the mantles exert a far less deleterious action on the amount of light than those of the thoria, which constitutes the main bulk of the heated mixture. T. H. P.

Gadolinium. By EUGÈNE DEMARÇAY (*Compt. rend.*, 1900, 131, 343—345).—The author has examined the spark spectrum of gadolinium magnesium nitrate containing only minute quantities of terbium, yttrium, and $\Sigma - \text{Z}_e$, and has determined the wave-lengths and relative intensities (maximum = 16) of 108 lines, which are given in the paper. The two most persistent are 3549.3 and 3545.7 with intensities of 10.5

and 10 respectively. Estimations of the atomic weight yield a number approximately the same as that obtained by previous observers, $Gd = 155$.
C. H. B.

Action of Sodium Thiosulphate on Potassium Antimony Tartrate. By FR. FAKTOR (*Chem. Centr.*, 1900, i, 1211; from *Pharm. Post*, 1900, 33, 233—234).—When a cold solution of potassium antimonyl tartrate is added to a cold solution of sodium thiosulphate and the mixture boiled, a compound, $SbSO_2$, separates as a bright red precipitate which may be washed with water, alcohol, and carbon disulphide, and dried at 100° ; the yield amounts to 5 per cent. of the tartrate used. When suspended in water, this compound is not attacked by hydrogen sulphide even at 80° , but when exposed to sunlight it shrinks in volume, becomes of a darker colour, and then has the composition Sb_2SO_4 . A brown precipitate, Sb_2SO_5 , is also obtained by mixing boiling solutions of potassium antimonyl tartrate and sodium thiosulphate.
E. W. W.

Mineralogical Chemistry.

Possibility of the Transference of Metals in Igneous Rocks through the Agency of Carbon Monoxide. By CLEMENS WINKLER (*Chem. Centr.*, 1900, i, 1307; from *Ber. k. sächs. Ges., Math.-phys. Kl.*, 1900, 52, 9—16).—It is suggested that the native iron found in the basalt of Disko Island, W. Greenland, may have been formed from iron and nickel carbonyls.

L. J. S.

Statement of Rock Analyses. By HENRY S. WASHINGTON (*Amer. J. Sci.*, 1900, [iv], 10, 59—63).—In order to introduce uniformity in the statement of rock analyses, so that the chemical character of a rock may be seen at a glance, it is suggested that the constituents be given in the following order, commencing with the eight principal oxides in the main portion of the analysis: SiO_2 , Al_2O_3 , Fe_2O_3 , FeO , MgO , CaO , Na_2O , K_2O , H_2O (ignition), H_2O (110°), CO_2 , TiO_2 , ZrO_2 , P_2O_5 , SO_3 , Cl, F, S (FeS_2), Cr_2O_3 , NiO, CoO, MnO, BaO, SrO, Li_2O .

L. J. S.

Calorimetric Examination of Pyrites and Marcasite. By ALFRED CAVAZZI (*Zeit. Kryst. Min.*, 1900, 32, 515; from *Rend. R. Accad. Sci. Ist. Bologna*, 1898, N.S. 2, 205—209).—The heat of combustion of pyrites and of marcasite is 1550 small calories for each mineral. Analyses of the material used gave:

	S.	Fe.	Si.	Total.
Pyrites	47.53	52.09	0.30	99.92
Marcasite	47.56	52.17	0.22	99.95

L. J. S.

Sulpharsenites of Lead from the Binnenthal. By RICHARD H. SOLLY, with Analyses by HENRY JACKSON (*Min. Mag.*, 1900, 12, 282—297).—An historical account is given of the minerals sartorite, rathite, dufrenoyite, and jordanite which occur in the white saccharoidal dolomite of the Binnenthal in Switzerland, and a detailed crystallographic account is given of jordanite. The following new analyses, made only on crystals, lead to the formulæ: sartorite, $\text{PbS}, \text{As}_2\text{S}_3$ (compare Abstr., 1896, ii, 109); rathite, $3\text{PbS}, 2\text{As}_2\text{S}_3$ (compare Abstr., 1896, ii, 659); jordanite, $4\text{PbS}, \text{As}_2\text{S}_3$. A collection is given of all the previously published analyses of these minerals; several, which were made on massive material, are placed under rathite, since they approximate to the new formula, $3\text{PbS}, 2\text{As}_2\text{S}_3$, given above.

	Pb.	S.	As.	Sb.	Fe.	Total.	Sp. gr.
Sartorite...	43·24	25·81	30·80	—	—	99·85	4·980
„ ...	43·93	25·60	30·46	—	—	99·99	—
„ ...	43·72	25·12	30·12	—	—	98·96	—
Rathite.....	51·51	23·41	24·62	—	—	99·54	5·412
„ ...	51·62	23·64	24·91	—	—	100·15	5·421
„ ...	52·43	24·12	21·96	0·43	0·33	99·27	—
Jordanite...	68·61	18·19	12·32	—	—	99·12	6·413
„ ...	68·83	18·42	12·46	—	—	99·71	—

L. J. S.

Carnotite and Associated Vanadiferous Minerals in Western Colorado. By WILLIAM F. HILLEBRAND and F. LESLIE RANSOME (*Amer. J. Sci.*, 1900, [iv], 10, 120—144).—Ores of uranium and vanadium occur as yellow and green impregnations in sandstone over a wide area in Western Colorado; one, of a bright yellow colour, has been described by C. Friedel and Cumenge under the name carnotite (Abstr., 1899, ii, 434), of which the composition was given as $2\text{U}_2\text{O}_3, \text{V}_2\text{O}_5, \text{K}_2\text{O}, 3\text{H}_2\text{O}$. In the present paper, the mode of occurrence is described, and several very detailed analyses are given, which, however, show considerable variations and do not confirm the above formula. Under I is given the maximum and minimum amounts of the more important constituents in six recalculated analyses made on the portion of the carnotite ore which is readily soluble in cold dilute nitric acid. The important constituents of the less soluble portion, given under II, show this to be a vanadiferous silicate, possibly allied to roscoelite. Carnotite is therefore a mixture of minerals.

The green colouring and cementing matter of certain sandstones near Placerville resembles roscoelite in composition, but it has less vanadium and more aluminium; the more important constituents in the recalculated analysis are given under III. The colouring matter in other green sandstones in the same region was found to be due to chromium.

	SiO_2 .	UO_3 .	V_2O_5 .	V_2O_3 .	Al_2O_3 .	Fe_2O_3 .	CaO .	BaO .	MgO .	K_2O .	H O .
I. {	—	58·75	19·85	—	—	—	2·10	0·83	0·16	4·33	5·08
	—	61·53	21·09	—	—	—	4·70	3·64	0·31	8·39	10·54
II.	43·94	—	—	6·54	16·58	5·93	0·24	—	4·43	3·70	18·44
III.	46·06	—	—	12·84	22·55	0·73	0·44	1·35	0·92	8·84	6·05

L. J. S.

Vanadinite (Endlichite) from Hillsboro', New Mexico. By VICTOR GOLDSCHMIDT (*Zeit. Kryst. Min.*, 1900, **32**, 561—578).—A detailed crystallographic description is given of the sulphur-yellow crystals of "endlichite" from Hillsboro', New Mexico. They have the same degree of symmetry (hexagonal with pyramidal hemihedrism), and very nearly the same axial ratio [$a:c=1:0.7126$] as ordinary vanadinite. Analyses by P. Jannasch of the tabular and of the columnar crystals gave the results under I and II respectively, agreeing with those required for the vanadinite formula $3\text{Pb}_3\text{V}_2\text{O}_8 + \text{PbCl}_2$. In I, the ratio $\text{V}_2\text{O}_5:\text{As}_2\text{O}_5$ is 8.6:1, and in II it is 11.7:1.

	PbO.	V ₂ O ₅ .	As ₂ O ₅ .	P ₂ O ₅ .	PbCl ₂ .	Total.	Sp. gr.
I.	69.30	17.66	2.60	0.35	9.98	99.89	6.88
II.	68.61	18.94	2.03	trace	9.73	99.31	6.88

L. J. S.

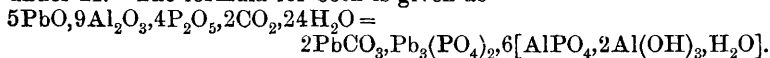
Perowskite from S. Ambrogio in the Valley of the Susa. By GIOVANNI BOERIS (*Atti Real. Accad. Lincei*, 1900, [v], **9**, i, 52—55).—A description is given of perowskite crystals found in the zone of contact between the granite and the serpentine of S. Ambrogio. Analysis gave TiO_2 , 58.63; FeO , 0.86; CaO , 40.29, total, 99.78; formula, CaTiO_3 ; hardness between 5 and 6; sp. gr., 3.98. The colour varied from a honey-yellow through yellowish-brown to almost black. The mineral is accompanied by chlorite, apatite, magnetite, and ilmenite.

T. H. P.

Larderellite from the Suffioni of Tuscany. By GIOVANNI D'ACHIARDI (*Atti Real. Accad. Lincei*, 1900, [v], **9**, i, 342—345).—Analysis of larderellite gives the following mean numbers: B_2O_3 , 72.06; $(\text{NH}_4)_2\text{O}$, 9.83; H_2O , 18.11 per cent. This indicates the formula $(\text{NH}_4)_2\text{B}_{10}\text{O}_{16}\cdot 5\text{H}_2\text{O}$, differing only in the water of crystallisation from the octahydrated ammonium pentaborate described by Rammelsberg in 1855. The specimen examined by Bechi, to which the formula $(\text{NH}_4)_2\text{B}_8\text{O}_{13}\cdot 4\text{H}_2\text{O}$ was given, probably contained impurities.

T. H. P.

Plumbogummite and Hitchcockite. By ERNALD GEORGE JUSTINIAN HARTLEY (*Min. Mag.*, 1900, **12**, 223—233).—There is a want of agreement in the old analyses of the poorly crystallised lead aluminium phosphates, plumbogummite and hitchcockite; the following new analyses have therefore been made on carefully selected material. The pale lavender to bright smalt-blue material, formerly considered to be calamine, which encrusts quartz and pyromorphite from the old Roughten Gill lead mines near Caldbeck, Cumberland, gave analysis I; traces of copper and arsenic are also present; no water is lost at 100° . This agrees in composition with the white hitchcockite from Canton mine, Georgia, of which a new analysis is given under II. The formula for both is given as



Dark brown plumbogummite from Huelgoat, Brittany, gave the results under III and IV; about 1 per cent. of organic matter is present.

Deducting the amount of pyromorphite corresponding with the chlorine, and also lead sulphate and about 5 per cent. of water lost at 100°, the remainder agrees approximately with the formula given above. Associated with the dark mineral from Huelgoat is a lighter coloured crystalline material (anal. V) with some minute crystals having the form of pyromorphite; this is mainly pyromorphite with some lead aluminium phosphate.

	PbO.	Al ₂ O ₃ .	P ₂ O ₅ .	CO ₂ .	H ₂ O.	Cl.	Insol.	Total.
I.	37.03	28.74	18.64	3.12	12.73	—	—	100.26
II.	34.36	29.48	17.58	2.77	14.71	—	0.82	99.72
III.	43.24	19.04	18.37	4.59	14.50	0.29	—	100.03
IV.	38.91	20.98	19.14	4.66	15.44	0.16	SO ₃ 0.96	100.25
V.	75.93	2.78	16.81	0.44	1.96	2.32	—	100.24

Hitchcockite (from Georgia and Cumberland) therefore appears to be a definite mineral, and plumbogummite (from Huelgoat) to be a mixture of hitchcockite and pyromorphite. L. J. S.

Beudantite. By ERNALD GEORGE JUSTINIAN HARTLEY (*Min. Mag.*, 1900, 12, 234—238).—The old analyses of beudantite differ so much that it is impossible to deduce any simple formula from them. The following new analysis was made on pure, dark green crystals supposed to be from the Glandore iron mines, Co. Cork (but possibly from Dernbach, Nassau). The material is soluble in strong hydrochloric acid. The formula is given as 3PbO, 4Fe₂O₃, P₂O₅, 3SO₃, 9H₂O = 3PbSO₄, 2FePO₄, 6Fe(OH)₃. Details of the method of analysis are given, and previous analyses are discussed.

PbO.	CuO.	Fe ₂ O ₃ .	P ₂ O ₅ .	As ₂ O ₅ .	SO ₃ .	H ₂ O.	Insol.	Total.
32.33	1.35	34.61	9.53	trace	12.72	8.45	0.56	99.37

L. J. S.

Florencite, a New Mineral from Brazil. By EUGEN HUSSAK and GEORGE T. PRIOR (*Min. Mag.*, 1900, 12, 244—248).—This new mineral has been found at three localities in Minas Geraes, namely, in the cinnabar-bearing sands of Tripuhy, in mica-schist near Tripuhy, and in diamond-bearing sands near Diamantina. The pale yellow crystals have a greasy to resinous lustre; they are rhombohedral [$a : c = 1 : 1.1901$] with a fairly perfect basal cleavage. $H = 5$; sp. gr. 3.586; optically uniaxial and positive. Analysis gave:

Al ₂ O ₃ .	Ce earths.	Fe ₂ O ₃ .	CaO.	SiO ₂ .	P ₂ O ₅ .	H ₂ O.	F.	Total.
32.28	28.00	0.76	1.31	0.48	25.61	10.87	undet.	99.31

Water is only given off at a high temperature. The molecular weight of the cerium earths is 352, which is considerably higher than usually accepted; didymium appears to be present in only small amount. The formula is given as 3Al₂O₃, Ce₂O₃, 2P₂O₅, 6H₂O = AlPO₄, CePO₄, Al₂(OH)₆.

Florencite is related crystallographically and chemically to hamlinite, 3Al₂O₃, 2(Sr, Ba)O, 2P₂O₅, 7H₂O (Abstr., 1898, ii, 123), and the two minerals are isomorphous, the strontium and barium of hamlinite

being replaced in florencite by cerium earths. These results support the conclusions of Wyruboff and others (Abstr., 1897, ii, 176) as to the isomorphism of many cerium salts with the corresponding salts of calcium and strontium, and the possible dyad character of the cerium earths.
L. J. S.

The Hamlinite-Florencite Group of Minerals. By GEORGE T. PRIOR (*Min. Mag.*, 1900, 12, 249—254).—It is pointed out that, owing to the difficulty of obtaining pure material and to imperfect methods of analysis and separation, mineral analyses are not so trustworthy as they are sometimes supposed to be when complex formulæ are deduced, and that when group relations can be made out, a more simple formula is sometimes preferable. On these grounds, it is suggested that hamlinite, florencite (preceding abstract), hitchcockite (this vol., ii, 600), beudantite (this vol., ii, 601), and svanbergite belong to the same isomorphous group of rhombohedral minerals, with the following formulæ and crystallographic constants:

	$a : c.$
Hamlinite, $2\text{SrO}, 3\text{Al}_2\text{O}_3, 2\text{P}_2\text{O}_5, 7\text{H}_2\text{O}$	1.1353
Svanbergite, $2\text{SrO}, 3\text{Al}_2\text{O}_3, \text{P}_2\text{O}_5, 2\text{SO}_3, 6\text{H}_2\text{O}$	1.2063
Hitchcockite, $2\text{PbO}, 3\text{Al}_2\text{O}_3, 2\text{P}_2\text{O}_5, 7\text{H}_2\text{O}$	—
Beudantite, $2\text{PbO}, 3\text{Fe}_2\text{O}_3, \text{P}_2\text{O}_5, 2\text{SO}_3, 6\text{H}_2\text{O}$	1.1842
Florencite, $\text{Ce}_2\text{O}_3, 3\text{Al}_2\text{O}_3, 2\text{P}_2\text{O}_5, 6\text{H}_2\text{O}$	1.1901

Here the group 2SO_3 is considered to be capable of replacing P_2O_5 without affecting the crystalline form; or writing hamlinite in the form $\text{SrHPO}_4, \text{AlPO}_4, \text{Al}_2(\text{OH})_6$, that is, as an ortho- instead of a pyrophosphate, the grouping SrHPO_4 may be considered as replaced in beudantite by PbSO_4 , in svanbergite by SrSO_4 , and in florencite by CePO_4 .

A new examination of svanbergite proves that the alkaline earth is mainly strontium and not calcium, as given in Blomstrand's analysis.
L. J. S.

Interpretation of Mineral Analyses: Constitution of Tourmaline. By SAMUEL L. PENFIELD (*Amer. J. Sci.*, 1900, [iv], 10, 19—32. Compare Abstr., 1899, ii, 304).—A reply to the criticisms of Clarke and Tschermak (Abstr., 1899, ii, 767; this vol., ii, 217). General remarks are made on the difficulties encountered in the analysis of minerals. Instead of deducing complex formulæ to suit particular analyses, it is better to assume the presence of some impurity.
L. J. S.

Asbestos [and Chrysotile]. By E. VAN DER BELLEN (*Chem. Zeit.*, 1900, 24, 392—393).—Light blue asbestos, in fibres 5—10 cm. long, gave on analysis the results under I, melting point 1150° ; hydrochloric acid (sp. gr. 1.124) dissolves 5 per cent. without destroying the silky lustre of the material. Greenish-brown "asbestos" [chrysotile], in fibres averaging 1 cm. long, gave II, agreeing with the serpentine formula $3\text{MgO}, 2\text{SiO}_2, 2\text{H}_2\text{O}$; melting point $1550\text{—}1570^\circ$; hydrochloric acid dissolves 57 per cent., leaving a residue consisting only of silica.

	SiO ₂ .	Al ₂ O ₃ .	Fe ₂ O ₃ .	FeO.	CaO.	MgO.	K ₂ O(Na ₂ O).	H ₂ O.	SO ₃ .
I.	56.79	3.85	8.03	—	1.00	20.48	5.93	3.73	0.59
II.	42.09	—	—	1.72	0.29	42.16	0.32	13.59	—

L. J. S.

Lasur-Oligoclase from Lake Baikal. By PAVEL V. VON JEREMEEFF (*Zeit. Kryst. Min.*, 1900, 32, 493—496).—These crystallographic notes on lasur-oligoclase, albite, and sphene from the neighbourhood of Lake Baikal were published in Russian in 1873, and are now for the first time given in German. The first-mentioned mineral was described by Nordenskiöld in 1857 under the name "Lasur-Felspath" as a variety of orthoclase, but the present author finds that the crystallographic elements agree closely with those of oligoclase, and he proposes the name "Lasur-oligoklas." The crystals are colourless to white with blue spots; some are decomposed and contain enclosures of calcite. Sp. gr. 2.587—2.598. Analysis gave:

SiO ₂ .	Al ₂ O ₃ .	CaO.	MgO.	Na ₂ O.	K ₂ O.	H ₂ O.	CO ₂ .	Total.
52.80	22.90	4.67	3.82	7.75	trace	3.66	3.90	99.50

L. J. S.

Sanidine from Monte Cimino, Rome. By FERRUCCIO ZAMBONINI (*Zeit. Kryst. Min.*, 1900, 32, 533—534; from *Rivista Min. Crist. Ital.*, 1898, 20, 20—64).—A description is given of crystals of Sanidine from Monte Cimino, near Viterbo. Regular intergrowths of sanidine with black mica or with augite occur. Analysis gave:

SiO ₂ .	Al ₂ O ₃ .	Fe ₂ O ₃ .	K ₂ O.	Na ₂ O.	CaO.	MgO.	TiO ₂ .	Total.
65.20	18.51	0.41	11.37	3.40	0.65	1.23	0.12	100.89

The TiO₂, MgO, and Fe₂O₃ are probably due to enclosures of sphene and mica.

L. J. S.

Stokesite, a New Mineral from Cornwall. By ARTHUR HUTCHINSON (*Min. Mag.*, 1900, 12, 274—281).—A preliminary account of this new mineral has already been published (this vol., ii, 89); a more complete description is now given. The locality at which the only crystal known was found is Roscommon Cliff, St. Just. From the results of two analyses made on small amounts of material, the composition is given as follows:

SiO ₂ .	SnO ₂ .	CaO.	H ₂ O.	Total.
43.1	33.3	13.45	8.6	98.45

At 220° there is a loss of 1.9 per cent., at 350° of 6 per cent., and the rest of the water is given off between 350° and dull redness. The formula H₄CaSnSi₃O₁₁ may be written in a variety of ways, as is the formula of catapleiite, H₄Na₂ZrSi₃O₁₁, in different text-books.

Stokesite is the first example of a well crystallised definite compound containing silica and stannic oxide as essential constituents.

L. J. S.

[**Hornblende and Anorthoclase.**] By E. C. E. LORD (*Zeit. Kryst. Min.*, 1900, 32, 602; from *Amer. Geologist*, 1898, 22, 335—346).—In a paper descriptive of the dykes in the vicinity of

Portland, Maine, the following mineral analyses are given. I, a hornblende (sp. gr. 3.47) resembling barkevikite from a camptonite dyke; II, anorthoclase from the same rock.

	SiO ₂ .	TiO ₂ .	Al ₂ O ₃ .	Fe ₂ O ₃ .	FeO.	CaO.	MgO.	Na ₂ O.	K ₂ O.	H ₂ O.	Total.
I.	37.80	4.54	12.89	6.14	12.55	13.64	4.10	5.26	3.24	—	100.16
II.	57.34	—	20.79	2.88	—	4.27	0.16	8.09	4.17	2.66	100.36

L. J. S.

Prehnite in Metamorphosed Limestone. By ALFRED LACROIX (*Compt. rend.*, 1900, 131, 69—72).—Prehnite (variety coupholite) is recorded as being associated with zoisite, grossular, and orthoclase in metamorphosed limestone in contact with granite, near Barèges, Haute-Pyrénées.

L. J. S.

Physiological Chemistry.

Elimination of Carbon Dioxide during Respiration. I. Influence of the Concentration of the Blood on the Tension of the Carbon Dioxide in it. By VALENTINO GRANDIS (*Atti Real. Accad. Lincei*, 1900, [v], 9, i, 130—137).—According to some observers, notably Pflüger, the phenomenon of gaseous exchange in the lungs obeys the laws of diffusion of gases, whilst others, among whom is C. Ludwig, hold that diffusion phenomena are incapable of explaining all the circumstances observed in the mutual relations of the gas in the lungs and ascribe to the epithelium of the pulmonary vesicles the power of secreting carbon dioxide and of absorbing oxygen. On bringing venous or arterial blood into contact with concentrated sugar or salt solutions in an apparatus designed to allow of the pressure being accurately measured by means of a water manometer, the author finds that, corresponding with the increase of the concentration of the blood, there occurs an increase in the pressure of the gas contained in the apparatus. It is hence concluded that, in the living animal, the concentration brought about in the blood circulating in the lungs by water being given up to the air in the lung passages causes a temporary increase in the pressure of the gas in the blood, with the result that a quantity of carbon dioxide is evolved greater than that corresponding with the pressure of this gas in the blood before concentration.
T. H. P.

Elimination of Carbon Dioxide during Respiration. II. Influence of the Hygrometric State on the Passage of Carbon Dioxide from the Blood to the Air. By VALENTINO GRANDIS (*Atti Real. Accad. Lincei*, 1900, [v], 9, i, 224—230. Compare preceding abstract).—A series of experiments, made on venous blood taken from the jugular vein of a dog, show that dry air is capable of withdrawing from blood a quantity of carbon dioxide greater than is the case with

air saturated with water vapour. Confirmation is thus lent to the conclusion (*loc. cit.*) that the concentration of the blood, when circulating in the lungs, causes an increase in the pressure of the contained gas. The experiments also show that one of the causes of the injurious effects of a moist climate on health is that the moisture of the air prevents the free escape of the gaseous products of metabolism from the blood.

T. H. P.

Temperature of the Body during Fasting and the Speed of Assimilation of Carbohydrates. By UGOLINO MOSSEO (*Atti Real. Accad. Lincei*, 1900, [v], 9, i, 77—84).—The temperature of a fasting dog shows after some days a gradual decline. Doses of 1—4 grams of sugar per kilogram of body weight cause the temperature of a fasting dog to rise rapidly in the first 10 or 15 minutes, the maximum being, however, reached in from 1 to 2 hours. The increase of temperature is maintained for a period of time directly proportional to the quantity of sugar administered. Sugar brings about the recovery of dogs in a critical state of hypothermia where the use of albumin is without effect.

Comparison of the effects of bread and sugar on the temperature of a fasting dog show that when the fast is of short duration and the temperature only slightly below the normal, the change is more rapid with bread than with sugar, the digestion still maintaining its activity. In the case of prolonged abstention from food, sugar causes the quicker rise of temperature. The quantities of bread and sugar required to produce a given heating effect are in the ratio 2 : 1.

T. H. P.

Rate of Absorption and of Assimilation of Proteids and Fats. By UGOLINO MOSSEO (*Atti Real. Accad. Lincei*, 1900, [v], 9, i, 122—129. Compare preceding abstract).—The effects caused by proteids and fats on the temperature of fasting dogs have been examined. The results show that veal and the constituents of yolk of egg are utilised only slowly in the production of heat, indicating that albumin and fat are mostly used in the formation of the tissues. Albumin does not serve as a means of keeping emaciated dogs alive, but this can be accomplished by administering sugar. Butter and pig's fat, like albumin, have no effect on the temperature of a well-fed dog when given in small quantities.

T. H. P.

Absorption of Fat. By LUDWIG HOFBAUER (*Pflüger's Archiv*, 1900, 81, 263—266).—A contribution towards the elucidation of the problem as to whether unsaponified fat can be absorbed. If all the fat of the food is absorbed in a form which is soluble in water, the fat globules in the epithelial cells and in the chyle should be colourless, if the fat has been previously coloured with pigments which are insoluble in water. If the fat particles remain coloured, then the fat globules of the emulsion must have been absorbed as such. The pigments used were alkana-red, and "Lackroth A," and in dogs it was found that the absorbed fat particles in cells and chyle were still red. They were never blue, although these pigments are turned blue by alkalis. A case of chyluria is referred to in which, after giving coloured fat, the fat particles in the urine were found to be coloured also.

W. D. H.

Pathological Fats. By ALONZO ENGLEBERT TAYLOR (*Pflüger's Archiv*, 1900, 81, 131—137).—Attention is directed to the results of others, who have failed to find an increase of fat in cases of phosphorus poisoning, and to the difference of opinion which exists in relation to the possibility of the formation of fat from proteid. In the present experiments, the liver fat in a case of acute yellow atrophy in man was found to contain 81 per cent. of olein and 3 per cent. of volatile fatty acids; the liver contained only traces of glycogen. In a series of cats, fatty infiltration of the kidney was produced by the use of sodium cantharidinate; the fat was compared with that of the healthy cat's kidney. The results are entirely negative as far as the question of the origin of the fats is concerned. The amount of fat from each pair of nephritic kidneys averaged 1·136 gram; from each pair of healthy kidneys, 1·640 gram. The most marked qualitative difference noted is an increase of olein in the pathological fat.

The following table gives the main results obtained; the normal fat was obtained from 12, the pathological from 9 pairs of kidneys.

	Normal fat.	Pathological fat.
Ether extract	19·686 gr.	11·230 gr.
Melting point of fatty acids	39·8°	34·7°
Acid number	6·8	12·9
Saponification number	218·8	178·8
Ether number	212	165·9
Reichert-Meissl number.....	5·7	3·6
Acetyl number	14·2	22·5
Olein per gram	0·3006 gr.	0·496 gr.
		W. D. H.

The Influence of "Saccharin" [o-Benzoisulphinide] on Digestion. By F. BERLIOZ (*Chem. Zeit.*, 1900, 24, 416—417).—The experiments on artificial gastric, and pancreatic digestion here recorded confirm those previously performed by Nencki (*Chem. Zeit. Repert.*, 1899, 23, 372), but are contrary to what has been stated by several previous experimenters. They show that "saccharin" does not hinder digestion.
W. D. H.

Phosphorus in Paranuclein from Casein. By HOLMES C. JACKSON (*Amer. J. Physiol.*, 1900, 4, 170—177).—The paranuclein, obtained by artificial gastric digestion from casein, contains phosphorus in organic combination. Chittenden's results in which the phosphorus recovered in the ash was equivalent to the total phosphorus of the paranuclein, are attributed to the large amount of ash in the products employed. If this is avoided and the formation of inorganic phosphates during ignition precluded, paranuclein yields over 2 per cent. of phosphorus.
W. D. H.

Influence of Experimental Modifications on the Consumption of Sugar. By ALBERT CHARRIN and A. GUILLEMONAT (*Compt. rend.*, 1900, 131, 126—128).—It has been previously shown in rabbits that the injection subcutaneously of a saline mixture increases their metabolic activity, whilst injection of various acids does the reverse. It

is now shown that if dextrose is injected as well, a certain quantity leaves the body by the urine, the remainder being utilised. The amount which is eliminated and the time during which the excretion lasts are increased greatly in the animals treated with acid.

W. D. H.

Behaviour of certain Artificial Hexoses in the Animal Body. By A. MÜNCH (*Zeit. physiol. Chem.*, 1900, 29, 493—516).—After the injection of formose into the jugular vein of rabbits, 71.5 per cent. appears unchanged in the urine. In well-fed rabbits, injection into the mesenteric vein causes glycosuria; the amount of glucose in the urine corresponds with that of formose injected. In starving rabbits, this does not occur, but about 11 per cent. of the formose appears unchanged in the urine. Formose serves to form glycogen, and thus may pass into the condition of dextrose. The digestive ferments have no action on it. Methose behaves qualitatively in the same way, but there are quantitative differences. The results with β -methylglucoside were also in the same direction.

W. D. H.

Uric Acid Formation after Splenectomy. By LAFAYETTE B. MENDEL and HOLMES C. JACKSON (*Amer. J. Physiol.*, 1900, 4, 163—169. Compare this vol., ii, 288).—Further experiments on dogs and cats are recorded, which show that the spleen has little or nothing to do with the production of uric acid. Experiments on the lymphatic glands are also negative.

W. D. H.

Results of the Extirpation of the Liver in Dogs. By SERGEI SALASKIN and J. ZALESKI (*Zeit. physiol. Chem.*, 1900, 29, 517—552).—The liver was removed in fourteen dogs; the urine was examined for nitrogen, urea, and ammonia. Full details of each experiment are given. Four animals died almost immediately; the majority between 5 and 6 hours later; one lived for 13 hours; the quantity of urine collected varied from 1.8 to 118.5 c.c. It had always an acid reaction; the percentage of urea sank, and that of ammonia rose, but these were not parallel. The blood and brain were also examined, but no rise of ammonia was found. There are thus differences between these results and those of Minkowski in geese. In dogs with an Eck's fistula, the toxic symptoms are due to accumulation of ammonia; in dogs with extirpated liver there is evidence of acid-poisoning.

W. D. H.

Proteolytic and Amylolytic Ferments in the Contents of the Human Colon. By JOHN C. HEMMETER (*Pflüger's Archiv*, 1900, 81, 151—166).—Extracts of human faeces, even in cases of atrophy of the stomach, have weak proteolytic, no lipolytic, and powerful amylolytic properties. The proteolytic ferment is not pepsin, as it will not act in an acid medium. The source of the ferments is probably the pancreas or the intestinal glands.

W. D. H.

Physico-chemical Relations of Animal Fluids and Tissues. By MAX OKER-BLOM (*Pflüger's Archiv*, 1900, 81, 167—221. Compare this vol., ii, 290, 356).—If potassium chloride, potassium sulphate, and

magnesium sulphate dissolved in serum are mixed with defibrinated ox-blood so that the osmotic pressure of the serum of the mixture is raised, they act on the blood corpuscles but little, whilst ammonium chloride and sulphate produce, under similar conditions, a marked effect. If aqueous solutions of potassium chloride or sulphate are mixed with the blood, they act on the corpuscles only when the osmotic pressure of their solutions is higher than that of the serum; they lose this property when the osmotic pressure of the serum is lowered. Magnesium sulphate in aqueous solution acts similarly. In the case of the ammonium salts, however, hypotonic as well as hypertonic solutions enter the corpuscles, but less forcibly. In all cases smaller quantities of the sulphates are necessary to produce the effects. These phenomena are related to that of electrical conductivity, which, although the method is but little used, forms a trustworthy guide to the power of electrolytes to penetrate the corpuscles. W. D. H.

Artificial Parthenogenesis. By JACQUES LOEB (*Amer. J. Physiol.*, 1900, 4, 178—184. Compare this vol., ii, 555).—Further experiments on this subject are stated to show that, by a certain increase in the osmotic pressure of the surrounding solution, the unfertilised eggs of some echinoderms can be caused to develop into normal blastulae or even plutei. This increase in osmotic pressure can be produced by electrolytes as well as by non-conductors. It is therefore probable that the parthenogenetic development is caused by the egg losing a certain amount of water. W. D. H.

Chemical Fertilisation of Eggs. By VIGNIER (*Compt. rend.*, 1900, 131, 118—121. Compare Loeb, this vol., ii, 555, and preceding abstract).—In a repetition of some of Loeb's experiments on the development of echinoid eggs, no grounds were found for believing his theory that any egg can develop parthenogenetically provided it is supplied with appropriate saline mixtures. In fact, magnesium chloride was found to hinder rather than favour development. Before accepting such sweeping ideas, it is necessary to show that the instances examined by Loeb were not accidental cases of true parthenogenesis. W. D. H.

Further Experiments on Tetanus Toxin and Antitoxin. By F. RANSOM (*Zeit. physiol. Chem.*, 1900, 29, 553—567. Compare this vol., ii, 558).—Antitoxic dog serum, like that of the horse, when injected into the blood-stream of dogs, divides itself between blood and lymph. Some time after the injection, there may be twice as much in the blood as in the lymph. The tetanus toxin, like the antitoxin, after being injected subcutaneously, passes into the blood *via* the lymph, but in the case of the toxin this takes place with great slowness. If the toxin is already in the blood and lymph, it is rapidly neutralised by injection of the antitoxin into the blood or lymph stream. W. D. H.

Composition of the Placenta: Its Solid and Liquid Components, Organic Compounds, Extractive Matter, and Albumoses. By VALENTINO GRANDIS (*Atti Real. Accad. Lincei*, 1900, [v], 9, i, 170—176).—The placenta was freed quickly from membrane and, after as much blood as possible had been removed, it was pounded into

a paste. On drying and igniting this paste, the mean numbers obtained were: dry substance, 16.09; water, 83.89; ash, 1.073 per cent. Extraction with water at 35° and removal of the albumin by coagulation gave the numbers: extractive matter, 1.925; dry albumin, 5.783; ash of albumin, 0.072. Further extraction under 2 atmospheres pressure removed 3.654 per cent., the insoluble residue amounting to 3.607 per cent. The water used for washing the placenta gave, on analysis: dry albumin, 1.37 and 2.16; ash, 0.017 and 0.064; whilst the red globules removed from the wash water gave: dry albumin, 1.58 and 2.39; ash, 0.017 and 0.024. These values, which vary very widely owing to the different amounts of blood retained, are calculated on the original weight of placenta. T. H. P.

Composition of the Ash of the Placenta. By VALENTINO GRANDIS (*Atti Real. Accad. Lincei*, 1900, [v], 9, i, 262—266. Compare preceding abstract).—Analysis of the ash of the placenta gives the following percentages: Cl, 11.4; S, 0.204; Na, 24.93; K, 6.57; PO_4 , 33.46; CaO , 2.32. The ash of the albumin extracted by water from the placenta contains Na, 0.251 and PO_4 , 55.18 per cent., whilst after previously washing the placenta with a 0.75 per cent. sodium chloride solution, the numbers are Na, 0.728, and PO_4 , 44.5. The large proportion of phosphorus seems to indicate that the placenta fulfils a more important function than that of a mere mechanical organ of communication between the mother and the foetus. It is noteworthy that the phosphorus is contained in substances which are extracted by water and are also precipitated together with the albumin from the aqueous solution. T. H. P.

Some Scientific and Ethical Questions of Biological Chemistry. By JOHN LEWIS W. THUDICHUM (*J. pr. Chem.*, 1900, [ii], 61, 568—575).—A controversial paper.

Chemistry of Vegetable Physiology and Agriculture.

Composition of Plankton. By K. BRANDT (*Bied. Centr.*, 1900, 29, 423; from *Naturw. Wochenschr.*, 1898, 13, 594).—Samples of plankton, and of its single constituents, obtained from Kiel Bay, were found to have the following composition :

	Proteids.	Fat.	Non-nitrog. extract.	Crude fibre.	Ash.
Plankton (autumn and winter) ...	20·2—21·8	2·1—3·2	60·0—68·9	8·5—15·7	
Peridineæ	13·0	1·3	39·0	41·5	5·2
Diatoms	28·7	8·0	63·2	—	—

Samples of summer plankton consisted chiefly of animals and contained therefore a high percentage of proteids and not much carbohydrate; the amounts of fat varied considerably. N. H. J. M.

Influence of the Temperature of Liquid Air on Bacteria. By ALLAN MACFADYEN (*Proc. Roy. Soc.*, 1900, 66, 180—182, and with SYDNEY ROWLAND, 339—340).—In the first set of experiments, pure cultivations of ten organisms, including the very sensitive spirillum of *Cholera Asiatica* and the highly resistant spores of *Bacillus anthracis*, were exposed for 20 hours at the temperature of -182° to -190° . The bacteria lost none of their vital properties. The photogenic bacteria became non-luminous when cooled down, but their luminosity was restored as the temperature was allowed to rise. A sample of yeast cell plasma also was not altered by being subjected for 20 hours to the same temperature.

In the second series, broth emulsion cultures sealed in fine quill tubing were completely immersed in liquid air for 7 days. The vitality of the organisms was in no way impaired. N. H. J. M.

Influence of the Temperature of Liquid Hydrogen on Bacteria. By ALLAN MACFADYEN and SYDNEY ROWLAND (*Proc. Roy. Soc.*, 1900, 66, 488—489. Compare preceding abstract).—Exposure for 10 hours at a temperature of about -252° had no effect on the following organisms: *Bacillus acidi lacti*, *B. typhosus*, *B. diphtheriae*, *Proteus vulgaris*, *B. anthracis*, *B. coli com.*, *Staphylococcus pyogenes aureus*, *Spirillum cholerae*, *B. phosphorescens*, *B. pyocyaneus*, a *Sarcina*, and a yeast. N. H. J. M.

Present Position of the Nitragin Question. By JULIUS STOKLASA (*Zeit. landw. Versuchswes. Oesterr.*, 1898, 1, 78—88).—Pure cultures of *Bacillus radicicola* promote the growth of leguminous plants, the amount of increase depending on the nature of the soil. The results of experiments in which lupin plants were deprived of their root-nodules, and afterwards grown in sterilised sand, indicated that fixation of nitrogen takes place, not in the nodules, but in the leaves. The bacteria seem to separate a kind of enzyme which causes the living protoplasm to assimilate elementary nitrogen. *B. radicicola* does not fix free nitrogen, but some species of fluorescence bacilli, which assimilate free nitrogen, were obtained from soil. N. H. J. M.

Further Observations on Nitragin, and the Nature and Functions of the Nodules of Leguminous Plants. By MARIA DAWSON (*Proc. Roy. Soc.*, 1900, 66, 63—65. Compare Abstr., 1899, ii, 785).—A study of the organisms from *Desmodium gyrans* showed they, as well as those from nitragin and from pea nodules, grow readily on gelatin or agar containing an extract of pea straw, asparagine, and sugar, but very slowly on broth-gelatin. They do not peptonise milk. The organisms are aerobic, and may pass through a short motile stage.

Addition of nitrate to sterilised cultures of plants gave better results than inoculation, whilst the inoculation of plants manured with nitrate decreased the yield. N. H. J. M.

Fermentation without Cells. By FELIX B. AHRENS (*Zeit. angew. Chem.*, 1900, 483—486).—Yeast extract may be concentrated by cooling to a temperature not lower than -2° , stirring and expressing the liquor from the resulting magma of crystals. By repeating this pro-

cess several times, the sp. gr. of the liquor may be raised from 1·0378 at 12° to 1·0765 at 14°. This concentrated extract gave satisfactory results in experiments where the original extract was too dilute. The author considers that zymase is present as a colloidal substance, and not in a state of true solution; that its loss of activity is due to acidity, which always develops in a few hours, and that the fluorescence, which disappears when the extract is kept or used as a fermenting agent, is caused by the zymase itself. Samples of the extract, in its original form and after concentration, were fractionally precipitated, the dried products analysed, and their percentage composition calculated on an ash-free basis. The carbon shows the greatest variation, but no discussion of the tabulated results is attempted.

R. L. J.

Furfuroids of Plant Tissues. By CHARLES FREDERICK CROSS, EDWARD JOHN BEVAN, and J. S. REMINGTON (*J. Soc. Chem. Ind.*, 1900, 19, 307—310).—Direct experiment has proved that hydrolysed furfuroids are almost completely digested and assimilated by herbivorous animals such as the rabbit. Previous researches have shown that in “the permanent tissue”—the residue from the solvent action of alkaline (sodium hydroxide) and acid (hydrochloric acid) solutions in the cold—the ratio of furfuroids to other carbohydrates is greater than in the total plant. After ensilage, the opposite is true; for example, a permanent tissue gave a furfuraldehyde number of 6·1 per cent., whereas the total furfuraldehyde was 9·3 per cent. On the other hand, however, the furfuroids show an increased resistance to processes of acid hydrolysis after ensilage.

J. J. S.

Nature of the Reserve Carbohydrates in the St. Ignatius Bean and Nux Vomica. By ÉMILE BOURQUELOT and J. LAURENT (*Compt. rend.*, 1900, 131, 276—278. Compare this vol., ii, 498).—The albumen of the St. Ignatius bean was heated for an hour and a half at 110°, under pressure, with dilute sulphuric acid containing from 1—3 per cent. of acid. The total quantity of sugar formed increased with the concentration of the acid, whilst the ratio of mannose to galactose varied considerably, the proportion of galactose being higher the more dilute the acid. When the albumen of *nux vomica* is heated for varying periods of time with acid of constant strength (1:100), the proportion of galactose increases considerably with the duration of heating. These results indicate that the two sugars are not derived from a single mannogalactan, or from one mannan and one galactan, but from several mannans and galactans of different degrees of complexity, analogous to the dextrans in starch.

C. H. B.

Dissolution of the Nitrogenous Compounds in Malt. By PAUL PETIT and G. LABOURASSE (*Compt. rend.*, 1900, 131, 349—351).—Malt was treated with water for two hours at different temperatures, and one-half of each infusion was boiled for some time, cooled, and made up to its original volume. Estimations were made in both the boiled and unboiled portions of the total nitrogen, the nitrogen precipitated by phosphotungstic acid and sulphate of zinc respectively, and the nitrogen existing as ammonia after treatment with dilute hydrochloric

acid. The total soluble nitrogen gradually increased with the temperature, and reached a maximum at 55°, whilst the coagulable compounds gradually decreased, and the total nitrogen also began to decrease at and beyond 62°. The sum of the various quantities of nitrogen separately estimated in the manner indicated was considerably greater than the total nitrogen actually present. The results with the un-boiled infusions were somewhat irregular, probably owing to the action of enzymes, and the action of hydrochloric acid on the insoluble compounds. With the boiled portions, the results were more regular; the nitrogen precipitated by phosphotungstic acid and zinc sulphate increased up to 45° and then decreased, whilst the total soluble nitrogen increased up to 55°, and then gradually diminished. Arginine is formed under conditions which will be described subsequently.

C. H. B.

Formation and Decomposition of Albumen in the Plant. By ERNST SCHULZE (*Chem. Centr.*, 1900, i, 1031—1032; from *Ber. Deut. bot. Ges.*, 18, 36—42).—The fact that in young *Papilionaceæ* which contain large quantities of the decomposition products of albumin the increase of albumin is not accompanied by any decrease in the amount of asparagine present, is explained by supposing that the initial decomposition products of albumin are converted into glutamine and asparagine. In accordance with this theory, the young plants were found to contain more of the primary decomposition products of albumin than the older plants. Whilst asparagine is of use in the synthesis of albumin in the plant, the amino-acids have not proved to be good substitutes.

E. W. W.

Formation of Proteids in Plants. By ADOLF EMMERLING (*Landw. Versuchs-Stat.*, 1900, 54, 215—281. Compare Abstr., 1887, 615).—Further evidence is adduced in favour of the hypothesis that amino-acids in plants are produced from simple inorganic nitrogen compounds and organic matter already formed by assimilation. The process takes place mainly in the leaves. As time goes on and the amount of amino-acids is in excess of that required for leaf production, the acids are utilised in the development of seeds. The amount of amino-acids gradually decreases when the seeds ripen, not only in the seeds themselves, but in the leaves, &c.

Simultaneously with the production of amino-acids, other nitrogenous non-proteids are formed the nature of which is not known. These compounds are less prominent than the amino-acids in nearly all parts of the plant during the chief period of the synthetical formation of amino-acids and proteids. But as the seeds ripen, the "bases," as these compounds are provisionally termed, increase in quantity and finally predominate over the amino-acids both in the seeds and in the leaves, &c. It is probable that the "bases" are of physiological importance, but there is as yet no evidence to show in what manner.

N. H. J. M.

Conditions of the Production of Proteids Insoluble in Gastric Juice and their Importance for the Respiration of Plants. By WLADIMIR PALLADIN (*Bied. Centr.*, 1900, 29, 478—481).—The proteids of the living substance of vegetable cells leave a nitro-

genous residue insoluble in gastric juice, whilst the "dead" proteids are dissolved.

Etiolated leaves of *Vicia faba* were kept for several days in 5 or 10 per cent. solutions of cane sugar, in darkness, in diffused daylight, and in yellow and blue light respectively. The amounts of dry matter, proteids, and indigestible proteids were determined as well as the amounts of carbon dioxide produced per hour.

The sugar was utilised much more readily in presence of light than in darkness, and the regeneration of proteids, which took place even in absence of light, was much more energetic in diffused light; blue light was more favourable than yellow. Undigestible proteids, which were present only in very small quantity in the etiolated leaves, were produced in the dark in presence of sugar, but the production was much greater under the influence of light.

The energy of respiration of leaves supplied with sugar was more than twice as great in presence of light than in darkness. It was greatest in white, and least in yellow light.

From the results of previous experiments (Abstr., 1898, ii, 248), it was concluded that the energy of respiration was directly proportional to the amount of "living proteid" at a given temperature and in presence of sufficient carbohydrate. It is now shown that there may be considerable variations.

N. H. J. M.

Germination of the Olive. By GIOVANNI SANI (*Atti Real. Accad. Lincei*, 1900, [v], 9, i, 47—51).—The constituents of olive seeds are as follows: Water, 9.82; fats, 42.00; reducing sugars after hydrolysis with 5 per cent. sulphuric acid, expressed in terms of glucose, 14.73; proteids (nitrogen $\times 6.25$), 17.02; ash, 2.87. After germinating for a week in the dark at 30°, the plantlets were dried at 110°, 10.63 per cent. of dry substance being obtained and analysed, the results being as follows: Fat, 6.23; reducing sugars present as such, in terms of dextrose, 4.60; further reducing sugars formed on hydrolysis, 26.34; pentosans, 9.51; nitrogen, 4.54. 1.3286 grams of the plants after treatment with water required 2 c.c. decinormal potassium hydroxide for neutralisation.

T. H. P.

Development and Injurious Effect of Mustard Oil from Rape-Cake. By B. SJOLLEMA (*Landw. Versuchs-Stat.*, 1900, 54, 311—318).—The introduction of an emulsion containing 0.2 gram of mustard oil into the stomach of a rabbit caused death. The same result was obtained by the simultaneous introduction of *Myronas Kalicus* (0.850 gram) and an extract of white mustard seed (6 grams). Both mustard seed and *Myronas Kalicus* were without effect when given alone. Mustard oil emulsion (0.2 gram), two days old, did not kill the rabbit, but otherwise produced the same symptoms. Another emulsion (0.3 gram), three weeks old, caused the death of the rabbit, but its action was slow.

The volatile oil, containing sulphur, which develops in rape seed by the action of an enzyme, is not identical with allylthiocarbimide and is much less poisonous. A rabbit which received 0.262 gram

of the oil showed no abnormal symptoms. The estimation of mustard oil in rape cake is, therefore, not to be depended on for ascertaining whether the cake is poisonous. The volatile oil obtained from rape boils at 173° , has an odour resembling that of mustard oil, but much less sharp, and floats on water. As regards the estimation of mustard oil, both the oxidation and Jörgensen's methods give somewhat low results.

Myrosin is rendered inactive by heating at 72° , but not at 65° . Neither pepsin alone nor pepsin and hydrochloric acid produce mustard oil from rape cake or *Myronas Kalicus*. Ptyalin acts with extreme slowness if at all. N. H. J. M.

Action of Calcium Hydroxide on Germination. By RICHARD WINDISCH (*Landw. Versuchs-Stat.*, 1900, 54, 283—309. Compare Sigmund, Abstr., 1896, ii, 442).—Solutions, or emulsions, containing 0.066—3.9642 per cent. of calcium hydroxide had very little effect on the germination of barley, oats, and wheat; in the case of rye, the number of seeds which germinated was somewhat reduced by the weakest solution. In a second series of experiments, the effect of solutions or emulsions containing 0.1724 to 5 per cent. of calcium hydroxide on the germination of a variety of seeds was observed. The results showed that the solutions affect chiefly the energy of germination, but that the extent of the action has no relation to the concentration of the solutions. The more dilute solutions have relatively more effect than the more concentrated ones. Only the dissolved hydroxide can penetrate into the cells; on the other hand, the undissolved lime seems to have some mechanical action, since seeds sometimes failed to germinate in emulsions when a saturated solution had no effect. Ordinary lime water, diluted with 2—3 parts of distilled water, was in some cases beneficial, and in others injurious. Wheat was not injured by the greatest amount of lime; oats germinated better in presence of lime than in distilled water; the germination of maize was somewhat delayed by concentrated solutions, whilst oats were injured.

Cruciferous seeds were injured by dilute lime water, and leguminous seeds, which are the most sensitive in this respect, were killed by comparatively dilute solutions. N. H. J. M.

Finnish Moss-Berry (*Vaccinium oxycoccus*). By F. STOLLE (*Zeit. Ver. Deut. Zuck.-Ind.*, 1900, 609—610).—The moss-berry of Finland, which is an extremely valuable food-stuff, yields, on crushing, about 74 per cent. of its weight of juice having a sp. gr. 1.0373. After the addition of ammoniacal lead acetate and concentration of the filtrate, invert sugar separates out. From the lead precipitate glyoxylic acid has been isolated. T. H. P.

Composition of Fodders. By ADOLF EMMERLING (*Bied. Centr.*, 1900, 29, 454—457; from *Jahresber. agrik.-chem. Versuchs-Stat. Kiel*, 1898, 15).—The results of fifty complete analyses of fodders (residues from oil factories and distilleries, molasses, meadow and clover hay, and straw, &c.) are given in tables. Also the results of determinations of proteid, fat, and acidity in a number of oil-cakes. N. H. J. M.

Changes in Expressed Olives when Stored under Different Conditions. By OTTO KLEIN (*Zeit. angew. Chem.*, 1900, 635—637).—Analyses were made of compressed olives kept under the following conditions: (1), air dried; (2), compressed in a covered glass vessel; (3), not compressed, and moistened with the expressed fruit-water; and (4), compressed and moistened with the fruit-water.

The results showed that in practice it is best to dry the residues as quickly as possible, or else to compress them with, or without, addition of the fruit-water. The loss of fat then is only slight.

Expressed olives are not of much value either as food or as manure, and to increase their value it is of importance to return the fruit-water, which contains much of the proteids and ash constituents. In this way a product is obtained the composition of which more nearly approaches that of olives.

Analyses of olives, expressed olives, and of the fruit-water are given.

N. H. J. M.

Experiments on Feeding Cows with Mixed Grain and Maize. By F. FRIS (*Bied. Centr.*, 1900, 29, 461—464; from *45-de Beretn. kgl. Vet. Landbohöjssk. Lab. landök. Forsög. Copenhagen*, 1899, 1—75).—The experiments were made at several farms with a large number of similar cows. Each group received cake, roots, hay, and straw, and in addition (A) mixed grain, (B) half mixed grain and half maize, and (C) maize.

Feeding with maize had no appreciable effect on the composition of the milk, but slightly increased the yield; there was also a slight increase in live weight. The butter from the cows fed with maize was of slightly better quality than when mixed grain was employed.

As regards the composition of the two foods the most important difference was in the amount of starch; the mixed grain contained 42.69, and the maize 56.74 per cent.

N. H. J. M.

Composition of the Alluvial Soil of Lodi. By FASCETTI and GHIGI (*Bied. Centr.*, 1900, 29, 421; from *Staz. sper. agrar. ital.*, 1899, 32, 131).—Analyses of the soil at different depths (0.5 m. to 3.1 m.) showed that it contained very little organic matter and nitrogen ($N=0.079$ to 0.019 per cent.), whilst the phosphoric acid, soluble in boiling hydrochloric acid, diminished from 0.194 at a depth of 0.5 m. to 0.125 per cent. in the lowest sample. The upper layers of the soil contained 0.61 — 0.70 per cent. of lime, and the lower layers 2.01 to 4.25 per cent. The amounts of potash dissolved by hydrochloric acid were 0.43 — 0.58 per cent. in the more sandy layers, whilst the layers with 10 or 11 per cent. of clay contained 0.70 — 0.84 per cent. of potash.

N. H. J. M.

Vegetation Experiments with Various Peat Soils. By HEINRICH IMMENDORFF and BRUNO TACKE (*Bied. Centr.*, 1900, 29, 443—446; from *Landw. Jahrb.*, 1898, 27, *Erg.-bd. IV.* 259—302).—The results of pot experiments with peat soil containing 2.52 — 3.39 per cent. of nitrogen showed that nitrogen manures were effective with oats, barley, and sugar-beet. The effect of nitrogenous manures is least in soils in which nitrification is most active, and this probably

depends to a great extent on the porosity of the soil, and the amount of water present. In the case of lighter soils, an excess of water is comparatively harmless, whilst dense soils are greatly injured. Light soils require, therefore, less drainage than dense soils.

The greatest yields of barley and oats were obtained when the soil was not quite saturated with water, but the greatest yield of nitrogen was observed under conditions of medium moisture. With oleaginous radish, the maximum yield was obtained under the same conditions; the maximum yield of nitrogen when the soil contained the greatest percentage of water. This is partly due to the greater evaporation from radishes.

Subsoil liming increased the yield of potatoes and oats by 16 and 18 per cent. respectively, whilst the yield of barley in field experiments was increased 70 per cent. (compare this vol., ii, 42). N. H. J. M.

Action of Animal Manure on Peat Soil. By PAUL HELLSTRÖM (*Bied. Centr.*, 1900, 29, 449—450; from *Tidskr. landtm.*, 1899, 20, 697—705).—Owing to the difficulties of obtaining lime and artificial manures in some parts of the north of Sweden, experiments were made to ascertain whether new peat land can be decomposed and thus rendered fertile by means of bacteria introduced along with farmyard manure, instead of by lime.

Peas were grown in zinc vessels and watered with extracts of horse-, sheep-, and cow-dung respectively. In each case, one pot had fresh and another sterilised extract. There were also two pots which had slaked lime, and two with soil alone.

All the extracts and the lime increased the yield of corn and straw; the fresh horse- and sheep-dung extracts were very much more effective than the same extracts sterilised. In the case of cow-dung extract, sterilisation had very little depressing effect. The results show, therefore, that horse- and sheep-dung are the best for peat land, not only as manures, but on account of the bacteria they contain. N. H. J. M.

Action of Burnt Lime and Marl on Sandy Soil. By BRUNO TACKE, HEINRICH IMMENDORFF, A. SALFELD, and FR. WOLFF (*Bied. Centr.*, 1900, 29, 448—449; from *Landw. Jahrb.*, 1898, *Erg.-bd. IV.*, 431).—When applied to the soil in the usual quantity, burnt lime does not injure the leguminous bacteria, but it acts with much greater vigour than marl on the nitrogenous constituents of the soil. In the case of poor sandy soil, marl is preferable to burnt lime.

The results of previous experiments in which lime seemed to act injuriously on the growth of the leguminous crop, whilst marl was not injurious, are now attributed partly to loss of soil nitrogen under the influence of lime, and partly to ineffective inoculation. The inoculation on the marled land was probably due to bacteria having been introduced along with the marl. N. H. J. M.

Top Dressing Experiments with Ammonium Sulphate and Sodium Nitrate. By KLÖPPER (*Bied. Centr.*, 1900, 29, 371—373; from Fühling's *Landw. Zeit.*, 1899, 114 and 138. Compare Abstr., 1899, ii, 512).—A reply to Wagner (Abstr., 1899, ii, 572) and Maercker (*Deut. landw. Presse*, 1898, No. 25 and 26).

The results of experiments with winter wheat, grown on heavy loam and on light sandy soils, in which the same amount of nitrogen was applied in the form of ammonium sulphate and as sodium nitrate, showed in each case a greater production of grain and straw under the influence of ammonium sulphate. The heavy soil contained 0.31 per cent. of lime and had previously been manured with dung, kainite and basic slag. The sandy soils contained 0.05 and 0.045 per cent. of lime.

In similar experiments with winter rye on loamy sand containing 0.62 per cent. of lime, sodium nitrate produced 17.5 kilos. more grain per hectare than ammonium sulphate, but 249 kilos. less straw. A second experiment with winter rye on soil containing 1.02 per cent. of lime showed that ammonium sulphate produced greater yields both of grain and straw (138 and 537 kilos.) than sodium nitrate.

Ammonium sulphate produced on the whole more grain than sodium nitrate, and the quality of the grain was better. N. H. J. M.

Sugar as an Aid to the Growth of Plants. By JOHN GOLDING (*J. Soc. Chem. Ind.*, 1900, 19, 324—325. Compare Abstr., 1899, ii, 689).—The results of sand-culture experiments with beans and lucerne showed that addition of sugar considerably increased the growth when the plants were inoculated. Sugar produced the same result with beans and sainfoin when the plants were manured with ammonium nitrate instead of being inoculated. Similar results were obtained in soil.

In absence of ammonium nitrate, or without inoculation, addition of sugar decreased the amount of produce, especially in the case of sainfoin and beans grown in sand.

Comparing the total yields of the different plants under the influence of inoculation and of combined nitrogen respectively, the results show in some cases inoculation, and in others nitrogenous manure to be the more effective.

Excess of sugar may kill the plants.

N. H. J. M.

Cultivation of Mulberry Trees. By V. ALPE (*Bied. Centr.*, 1900, 29, 422—423; from *Agric. Mod.*, 1899, 5, 121).—In the Italian method of cultivating mulberry trees the average quantity of wood and leaves removed yearly amounts to 20 and 25 kilos. respectively. The losses of manure constituents in the portions removed are as follows:—N, 510; P_2O_5 , 172; K_2O , 195, and CaO, 486 grams. The yearly application of 100 kilos. of farmyard manure to each tree supplies sufficient nitrogen and phosphoric acid, and an excess of potash. Artificial manures may be applied in the following amounts: Sodium nitrate, 3.5; 16 per cent. superphosphate, 1.1; and potassium chloride, 0.4 kilo. per tree per annum.

N. H. J. M.

Composition of the Gas Confined in Farmyard Manure. By PIERRE P. DEHERAIN and C. DUPONT (*Ann. Agron.*, 1900, 26, 273—294. Compare Abstr., 1884, 1412).—When farmyard manure is watered with liquid manure, carbon dioxide is rapidly produced even near the

surface, and if the damp condition of the manure is maintained there is practically no loss of ammonia.

Aërobic fermentation takes place at the surface when fresh litter is added to the heap; it is very active and causes the temperature to rise as high as 75° . When the manure contains less than 70 per cent. of moisture, aërobic fermentation extends, and oxygen is present in the lower portions of the heap. Decomposition of nitrogenous matter with elimination of free nitrogen may then take place. It is of importance for the manure to become consolidated either by being trampled on by cattle or by being watered with liquid manure.

Hydric fermentation occurs when air penetrates the manure with difficulty; nitrogen is sometimes liberated; carbon dioxide is often produced along with hydrogen, and this suggests that the liberation of hydrogen is accompanied by the production of acids, such as butyric and acetic, capable of decomposing carbonates. Hydrogen is only readily liberated when the manure is neutral or slightly acid, and is no longer produced when the manure is rendered alkaline by addition of liquid manure.

When manure is sufficiently consolidated to exclude air, carbon dioxide and methane alone are produced. Loss of nitrogen cannot take place, as even if nitrogenous matter is decomposed, ammonia alone will be produced and the great excess of carbon dioxide prevents the dissociation of the ammonium carbonate (compare Abstr., 1899, ii, 800).
N. H. J. M.

Phosphoric Acid in Presence of Saturated Solutions of Calcium Hydrogen Carbonate. By TH. SCHLOESING (*Compt. rend.*, 1900, 131, 211—215).—When a small quantity of phosphoric acid is added to a saturated solution of calcium carbonate in water containing carbon dioxide, there is no immediate precipitation, but if the carbon dioxide is expelled by means of a current of air, hydrated tricalcium phosphate is precipitated. Magnesium carbonate behaves in a similar manner.

If phosphoric acid is added in excess, the precipitate is a mixture of di- and tri-calcium phosphates, or consists of the crystallised dicalcium phosphate only, $\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$, which is somewhat soluble in water containing carbon dioxide, provided that calcium carbonate is not also present.

The author concludes that superphosphates, when applied to soils, become converted into insoluble tricalcium phosphate mainly by the action of water containing calcium carbonate in solution, either with or without carbon dioxide. On the other hand, phosphates in solution in natural waters become precipitated in the form of tricalcium phosphate when they percolate through rocks and soils containing calcium carbonate, or when they come in contact with water containing calcium carbonate in solution.
C. H. B.

Solubility of the Phosphoric Acid of Basic Slag and Crude Phosphates in Peat Soils. Dependence of the Solubility on the Amount of Free Humic Acid in the Soil. By H. MINNSEN and BRUNO TACKE (*Bied. Centr.*, 1900, 29, 447—448; from *Landw. Jahrb.*, 1898, *Erg.-bd.*, iv, 392).—The solubility of phosphoric acid

in peat soil depends on the amount of free humic acid present, and the application of lime in the usual amounts greatly diminishes the solubility of phosphoric acid, except in the case of basic slag.

The phosphoric acid of basic slag which is insoluble in citric acid is less soluble in peaty soil than that of crude phosphates, but seems to be more soluble in partially neutralised soil the more citrate-soluble the original slag.

Although the solubility of phosphates no doubt increases with increasing amounts of free humic acid in the soil, the numerical agreement is affected by the absorption by the soil of some of the phosphoric acid previously dissolved.

N. H. J. M.

Analytical Chemistry.

Examination of Sea Water by an Optical Method. By J. J. MANLEY (*Proc. Roy. Soc. Edin.*, 1900, 23, 35—43).—The relative densities and relative deviations of five samples of sea water of nearly equal total salinity have been determined. By relative deviation is meant the ratio S_D/W_D , where S_D and W_D are the minimum deviations of the D line by sea water and distilled water respectively, with a selected prism and at a standard temperature. The determination of relative deviations is recommended as a method of estimating the relative salinity of sea waters. The order of salinity of the five samples examined is the same whether the method of relative densities or relative deviations be employed; the latter method is at least as dependable, and much more rapid. J. C. P.

Qualitative Analysis of the Ammonium Sulphide Group. By FERDINAND JEAN (*Chem. Centr.*, 1900, i, 1104; from *Ann. Chim. anal. appl.*, 1900, 5, 125—128).—The scheme is intended for solutions containing nickel, cobalt, iron, zinc, chromium, manganese, aluminium, and phosphates, borates, or silicofluorides of barium, strontium, calcium, and magnesium. After removal of any metals precipitable by hydrogen sulphide, the filtrate is evaporated to dryness in a platinum dish and the residue heated with strong sulphuric acid; the mixture is diluted with water, an equal volume of alcohol added, and the sulphates of the alkaline earths and any silica from silicofluorides are filtered off.

The filtrate freed from alcohol is mixed with 20—25 c.c. of concentrated ammonium citrate solution, ammonium chloride, and excess of ammonia, and strongly shaken. A precipitate indicates phosphoric acid and magnesia. If no precipitate is formed, a portion of the mixture is tested with sodium phosphate for magnesia, and another portion with magnesium chloride for phosphoric acid. If phosphoric acid is present, it is completely precipitated by further addition of magnesium chloride, the filtrate evaporated and the residue calcined

in a platinum dish, dissolved in hydrochloric acid, and precipitated with ammonia and ammonium sulphide. This precipitate is treated with a mixture of 1 part of hydrochloric acid and 5 parts of water saturated with hydrogen sulphide which redissolves it with the exception of the sulphides of nickel and cobalt. The solution is heated with a little potassium chlorate and then boiled with excess of sodium hydroxide. Zinc is detected in the filtrate by means of hydrogen sulphide and aluminium by acidifying with hydrochloric acid and adding ammonia. A small portion of the precipitate caused by the sodium hydroxide is well washed and then tested for iron with potassium ferrocyanide. The other portion is boiled in a test-tube with nitric acid and lead dioxide; in the presence of manganese, it turns violet, and in the presence of chromium, yellow. In the first case, the filtered liquid is mixed with oxalic acid, which destroys the manganese colour and then shows any yellow colour due to chromium which may then be further tested with acetic acid and lead acetate; in the second case, the residue in the test-tube is washed a few times by decantation and boiled again with lead dioxide and nitric acid, when manganese will again give a violet colour.

The insoluble sulphates are repeatedly boiled with solution of sodium carbonate, and the residue is dissolved in hydrochloric acid. In one portion of the solution, barium is tested for by means of hydrofluosilicic acid; some alcohol is added and the filtrate examined for strontium by the flame-test. In another portion, any barium or strontium is precipitated with ammonium sulphate, and the filtrate is then tested for calcium with ammonium oxalate. L. DE K.

Standardising Normal Acids. By HERMANN THIELE and R. RICHTER (*Zeit. angew. Chem.*, 1900, 486—489).—The authors have noticed that when acids are standardised by means of Iceland spar, the results are slightly higher than when sodium carbonate is used. As the result of a lengthy investigation, using pure materials, they find themselves unable to account for this phenomenon. L. DE K.

Necessary Precautions in certain Acidimetric Estimations. By LOUIS MAGNIER DE LA SOURCE (*Chem. Centr.*, 1900, i, 1103—1104; from *Ann. Chim. anal. appl.*, 1900, 5, 121—125).—When titrating acids, using phenolphthalein as indicator, it is not a matter of indifference whether the operation is performed cold or hot, as the reaction is more sensitive in the cold. Moreover, some kinds of glass yield to hot water a distinct trace of alkali. When estimating sulphuric acid, it does not matter whether a strong or a more dilute solution is titrated, but when dealing with tartaric acid a strong solution should be used, otherwise the results will be too low. L. DE K.

Iodometric Experiments. By GUNNER JØRGENSEN (*Zeit. anorg. Chem.*, 1900, 24, 183—187).—The reaction between potassium iodate, sodium thiosulphate, and hydrochloric acid takes place according to the equations: $\text{KIO}_3 + 6\text{HCl} + 6\text{Na}_2\text{S}_2\text{O}_3 = \text{KI} + 6\text{NaCl} + 3\text{Na}_2\text{S}_4\text{O}_6 + 3\text{H}_2\text{O}$ and $4\text{KIO}_3 + 3\text{Na}_2\text{S}_2\text{O}_3 + 3\text{H}_2\text{O} + \text{HCl} = 4\text{KI} + 6\text{NaHSO}_4 + \text{HCl}$. The ratio between the amounts of sulphuric acid and tetrathionic acid is dependent on the time allowed for the reaction. The results con-

firm the author's earlier work (Abstr., 1899, ii, 248), and are not dependent on the formation of iodine chloride as stated by Fessel (Abstr., 1899, ii, 802), since it is immaterial whether sulphuric acid or hydrochloric acid is employed.

E. C. R.

Improvement in Péligré's Absorption Apparatus for Ammonia Estimations. By F. PANNERTZ (*Zeit. anal. Chem.*, 1900, 39, 318—320).—The lower bulb of the Péligré U-tube is connected by a narrow tube inserted at the top of the bulb with the upper part of the first limb of the U-tube. By this means, all regurgitation of the absorbing liquid, occasioned by sudden condensation in the distilling flask, is prevented.

M. J. S.

Estimation of Sulphur Dioxide in Sulphites and Thiosulphates. By MARTIN L. GRIFFIN (*J. Soc. Chem. Ind.*, 1900, 19, 321—323).—The author's experiments indicate that there is no need to strictly follow Bunsen's instructions regarding dilution when titrating sulphur dioxide with iodine, as it is oxidised equally satisfactorily in strong and weak solutions.

Sulphurous acid should be titrated in a closed bottle provided with a U-tube containing a little iodine solution and serving as a trap for any sulphur dioxide which may evaporate; there is but little fear of loss by oxidation. Some sulphites, notably the sodium salt, are so rapidly oxidised by atmospheric oxygen that they should be at once introduced into a vessel containing iodine solution without previous solution or dilution; the excess of iodine is then titrated with sodium thiosulphate.

L. DE K.

Detection of Nitrous Acid in Water. By H. MENNICKE (*Zeit. angew. Chem.*, 1900, 711—719).—The author has compared the relative sensitiveness of the reagents most frequently used for the detection and estimation of nitrous acid in water, namely, solutions of starch-potassium iodide or zinc iodide, the four modifications of Griess' reagent, Riegler's reagent, and Erdmann's reagent (this vol., ii, 243). The results are recorded in two tables, and the conclusion reached is that Erdmann's test is almost free from sources of error and the most delicate of those examined.

L. DE K.

Analysis of Nitric Acid and Mixed Acid [Nitric and Sulphuric]. By ARTHUR P. VAN GELDER (*J. Soc. Chem. Ind.*, 1900, 19, 508—509).—*Analysis of Nitric Acid.*—About 10 grams of the acid are weighed out in a bottle, which is then opened in a funnel under water, and the solution diluted to 1 litre. 100 c.c. of the solution are titrated with $N/3$ alkali, and the total acidity is calculated as nitric acid. To estimate the amount of the lower oxides, 10 c.c. of the original acid are diluted to 100 c.c., and titrated with $N/10$ permanganate.

Analysis of Mixed Acid.—In this case 100 c.c. of the solution are evaporated on a water-bath with the aid of a slight blast of air until the nitric acid has been driven off. A little boiling water is added, and the evaporation continued for 10 minutes; this is repeated three times so as to break up any combined nitrogen oxides. The residual liquid is then titrated, and the difference between the two titrations

represents the total nitric acid. The lower oxides are estimated as before, although the estimation may be interfered with by the presence of arsenic.

To obtain the original hydrogen nitrate in nitric and mixed acid, the amount of nitric acid corresponding with the nitrous acid found by titration with permanganate should be deducted from the total amount; to obtain the available nitric acid, only half the amount of nitrous acid should be allowed for.

L. DE K.

Elimination of Arsenic from the System from a Toxicological Standpoint. By D. SCHERBATSCHOFF (*Chem. Centr.*, 1900, i, 1040; from *Viertelj.-Schr. gerichtl. Med. u. Oeff. Sanitätsw.*, 1900, [iii], 19, 232—262).—Experiments with a rabbit and a dog showed that the arsenic was more rapidly eliminated from the system of the former than of the latter, hence no conclusion should be drawn as to what would happen in animals of a different species or in human beings.

The arsenic was tested for as follows: 20—30 grams of the substance were heated in a Kjeldahl flask with 20—30 c.c. of pure sulphuric acid and a little copper oxide, the solution was diluted with water, boiled to expel any sulphur dioxide (finally with addition of potassium permanganate), and then tested in Marsh's apparatus. When the substance contains much chlorides, some of the arsenic may volatilise; this may be prevented by moistening the mass first with ammonium sulphide, and then heating with a mixture of nitric and sulphuric acids.

L. DE K.

The Carbon Dioxide of the Atmosphere. By EDMUND A. LETTS and ROBERT F. BLAKE (*Sci. Proc. Roy. Dubl. Soc.*, 1900, N. S. 9, ii, 107—270).—In Pettenkofer's method for the estimation of carbon dioxide in the atmosphere, an important source of error is introduced by the employment of barium hydroxide, which, when kept in glass vessels, rapidly causes a superficial corrosion, and then becomes contaminated with alkalis and silica from the glass. The presence of the former causes an increase in alkalinity, and the latter interferes with the proper end reaction when titrating the excess of barium hydroxide, using phenolphthalein as indicator. Another source of error is the difficulty of preparing distilled water free from carbon dioxide, as the distillate from water rendered alkaline with sodium hydroxide rapidly absorbs it from the air. The chief source of error, however, leading to results about 30 per cent. too high, is caused by the absorption of carbon dioxide from the atmosphere and breath during the transfer of the absorbent from the receiver, and its subsequent titration in open vessels. The authors have succeeded in avoiding these sources of error by using the following process.

The standard barium hydroxide solution is preserved in a reservoir attached in the usual way to a bulb-shaped pipette delivering exactly 50 c.c., and provided with a stopcock. The reservoir is, as usual, provided with a soda-lime tube, which is closed when the apparatus is not being used. To prevent any action of the baryta on the glass, the inside of the reservoir, and also the lower part of the glass siphon tube, is coated with paraffin wax. The air to be examined is collected in a narrow-necked, tall jar holding about 6 litres, and also

coated inside with paraffin wax. Through the indiarubber cork pass two glass tubes, one of which is bent at a right angle, and both can be closed when required by plugs consisting of short glass rods attached to pieces of indiarubber tubing. The jar is filled by connecting it with an exhausting syringe attached to an indiarubber tube 12 feet long, so that there is no danger of the collecting area being contaminated by the breath of the operator. A pump is used which removes about 200 c.c. at each stroke, so when 100 strokes have been given, the air originally present in the bottle will have been completely displaced by the air to be tested. The plug of the straight tube is now temporarily replaced by a soda-lime tube, the rubber junction being pinched between the finger and thumb during the operation to prevent access of air. After removing the other plug with the same precaution, the rubber is connected with the pipette, and 50 c.c. of the baryta solution are introduced. After replacing the plugs with the same precautions, the receiving jar is placed on its side for some hours, and frequently rolled about so as to ensure complete absorption of the carbon dioxide.

The receiver is now inverted and clamped to a retort stand, a soda-lime tube attached to the straight tube, and the bent tube connected, with the usual precautions, to the titrating vessel. This consists of a ball-shaped, narrow-necked glass flask, furnished with a two-way stopcock, which communicates with a straight tube, and also with a bent tube, which may be connected with an air-pump. After exhausting the flask, it is connected with the receiving vessel, the stopcock is turned, and the liquid runs into the flask. The last traces of the liquid are removed as follows. The titrating vessel is first removed, and a glass-rod plug substituted for it. The receiver is unclamped and placed upright, and the nozzle of a measuring pipette filled with water containing a little phenolphthalein and carefully neutralised with barium hydroxide is now inserted instead of the plug. On opening the stopcock attached to the pipette, the water runs into the receiver, which, after being well rinsed, is again placed in the former position and connected with the titrating flask; the rinsings are then added in the way described.

The titrating flask is now connected with a delicate burette containing a solution of pure oxalic acid of such a strength that 1 c.c. represents 0.1 c.c. of carbon dioxide at N.T.P. The barium hydroxide solution, which should be titrated about the same time, should, if possible, correspond exactly in strength with the acid.

The test-analyses made with pure air mixed with definite volumes of carbon dioxide are very satisfactory.

The paper contains a summary and bibliography of previous work on the subject.

L. DE K.

Liquid Carbon Dioxide. By G. HOLSTE (*Zeit. anal. Chem.*, 1900, 39, 243—245; from *Zeit. gesamt. Kohlensäure Ind.*, 3, 461).—The principal gaseous impurities in commercial liquid carbon dioxide are nitrogen and oxygen, which remain gaseous in the storage cylinder. A sample of the gas taken when the cylinder is placed with the valve uppermost will therefore have a different composition from

one taken when the cylinder is inverted or laid horizontally. Both should be analysed. A convenient eudiometer for the purpose is described, and a method for calculating the average composition of the contents of the cylinder is given. M. J. S.

Preparation of Sodium Cobalt Nitrite, and its Employment for the Detection of Potassium. By EINAR BILLMANN (*Zeit. anal. Chem.*, 1900, 39, 284—289. Compare Adie and Wood, *Trans.*, 1900, 1076).—For the detection of potassium in presence of much sodium, a solution of pure sodium cobalt nitrite is more sensitive than the spectroscope itself. To prepare the reagent, 150 grams of sodium nitrite are dissolved in 150 c.c. of warm water, and the solution cooled to 40—50°; 50 grams of crystallised cobalt nitrate are added, and then gradually 50 c.c. of 50 per cent. acetic acid, the mixture being vigorously shaken. A brisk current of air is then passed through the mixture for half-an-hour. The mixture is allowed to subside during two hours, and then filtered. The clear filtrate and washings, amounting in all to 300 c.c., are precipitated by the gradual addition of 250 c.c. of 96 per cent. alcohol. The salt is collected on a suction filter, washed four times with 25 c.c. of alcohol, twice with 25 c.c. of ether, and air-dried. For use, 0.3—0.5 gram is dissolved in 2—3 c.c. of water, and added cold to the solution to be tested. This solution must contain only potassium and sodium as chlorides, nitrates or sulphates, and must be free from phosphates, mineral acids, or caustic alkalis. Small amounts of acetic acid, alkali carbonates, magnesium, and calcium salts do not greatly impair the sensitiveness. It is possible with this reagent to detect 0.0009 milligram of potassium in presence of 2363 parts of sodium. The reagent is not permanent when dissolved; the solution must be prepared when required.

M. J. S.

The Estimation of Zinc as Phosphate. By H. D. DAKIN (*Zeit. anal. Chem.*, 1900, 39, 273—284).—Guyard ["Hugo Tamm"], who first proposed the estimation of zinc as zinc ammonium phosphate (*Abstr.*, 1871, 1214), admitted the existence of several sources of error, and did not furnish proof analyses of pure substances. Austin, who supplied this deficiency (this vol., ii, 49), assumed that the presence of at least 10 per cent. of ammonium chloride in the solution was essential. The author, starting with zinc oxide purified with great care, shows by numerous proof analyses that accurate results can be obtained without the use of large quantities of ammonium chloride. The use of ammonium phosphate, instead of sodium phosphate, avoids the error caused by the presence of sodium in the precipitate. Traces of zinc can generally be detected in the filtrate by ammonium sulphide, but never more than 2—3 decimilligrams. The precipitate, dried for 2 hours at 100—105°, has the composition ZnNH_4PO_4 ; it suffers no loss by prolonged drying at this temperature, and can be accurately converted into zinc pyrophosphate by gradual heating in an open crucible. If rapidly exposed to a red heat, reduction takes place. The following method of precipitation is recommended. The acid zinc solution, in a platinum basin, is nearly neutralised with ammonia, diluted to 150 c.c., and heated on the water-bath. About 10 parts of ammonium

phosphate for each part of zinc supposed to be present are added, and the heating is continued for a quarter of an hour. After a little further delay ($\frac{1}{2}$ —24 hours) the precipitate is collected on an asbestos filter in a Gooch crucible, washed thoroughly with a hot 1 per cent. solution of ammonium phosphate, and the latter removed by several washings with aqueous alcohol. It is then dried and weighed, or, if ignition is preferred, the Gooch crucible is placed inside a platinum crucible. The precipitate is then removed from the filter by dilute nitric acid, and the crucible dried (or ignited) as before. This mode of obtaining the tare is preferable to weighing the crucible before filtration, as the phosphate solution slightly attacks the asbestos. The results were as accurate when only 1 gram of ammonium chloride was present, as with 10 or 20 grams. A large amount hastens the crystallisation of the precipitate, but introduces inconvenience in the washing.

M. J. S.

Detection of Sodium in the Presence of Potassium. By N. SCHOORL (*Chem. Centr.*, 1900, i, 1140; from *Ned. Tijdschr. Pharm.*, 1900, 12, 116—118).—The microchemical test for sodium by means of uranyl acetate is interfered with by the presence of much potassium. The author now proposes to evaporate a few times with perchloric acid, and then to extract with alcohol. Potassium perchlorate remains undissolved, and the filtrate contains the sodium which may then be tested for by the uranium method.

L. DE K.

Colour Reactions for Detecting Calcium Salts in Organic Tissues. By VALENTINO GRANDIS and C. MAININI (*Atti Real. Accad. Lincei*, 1900, [v], 9, i, 280—283).—The piece of tissue or section is placed in a saturated alcoholic solution of purpurin and left until it is strongly coloured, the time required being from 5 to 10 minutes. When removed from the solution, it is not uniformly coloured, but exhibits dark patches which are hard. These dark patches, due to the deposition of the colour on salts of calcium, usually the carbonate and phosphate, may be made clearer by immersion for a few moments in a 0.75 per cent. solution of sodium chloride, which causes the formation of a small quantity of calcium chloride and consequent precipitation of the purpurin in an insoluble form in those positions where calcium salts are present. The coloured tissue is then soaked several times in 70 per cent. alcohol until no more colour is removed.

The presence of calcium salts can also be localised by treating the well-washed tissue with pyrogallol, which is fixed specially on those parts where calcium salts are situated. After remaining in contact with the air for some time to allow the pyrogallol to oxidise, the tissue is washed quickly in water, dried, and preserved in balsam. The presence of calcium salts is denoted by dark brown patches, the remainder of the tissue having only a pale, brownish-yellow colour.

T. H. P.

Detection of Barium, Calcium, and Strontium, and the Action of Ammonium Chloride on Strontium Chromate. By ERNEST DUMESNIL (*Ann. Chim. Phys.*, 1900, [vii], 20, 125—135; *Zeit. Ver. Deut. Zuck.-Ind.*, 1900, 531—537).—The ordinary methods

for detecting the presence of barium, calcium, and strontium in mixtures of salts fail when the proportion of strontium is small. To obviate this difficulty, the following method is proposed. The precipitate, consisting of the mixed carbonates, is dissolved in the least possible quantity of 10 per cent. hydrochloric acid, the solution evaporated to dryness to expel excess of acid, and the residue dissolved in water. To a small portion of the solution, strontium chromate solution is added; the formation of a precipitate indicates the presence of barium. If no precipitate forms, another portion of the neutral liquid is mixed with calcium chromate solution, the formation of a precipitate on warming showing the presence of strontium. If baryta is present, however, the remainder of the neutral chloride solution is precipitated by means of potassium chromate, the liquid being then heated to boiling and filtered; the precipitate is then boiled for a few moments with ammonium chloride solution and filtered. To the clear filtrate sodium carbonate is added, the liquid filtered, the precipitate washed once on the filter, and then treated with 10 per cent. acetic acid. Part of the liquid thus obtained is neutralised with ammonia and then warmed with calcium chromate solution; the formation of a precipitate shows the presence of strontium. Another part of the acetic acid solution is heated with an acetic acid solution of strontium oxalate, by which means any calcium is precipitated.

Ammonium chloride solution dissolves strontium chromate, and the solution deposits orange-yellow, tabular crystals having a composition corresponding with the formula $2(\text{NH}_4)_2\text{Cr}_2\text{O}_7 \cdot \text{NH}_4\text{Cl}$. T. H. P.

Action of Carbon Dioxide on the Borates of Barium. By HARMON N. MORSE and D. W. HORN (*Amer. Chem. J.*, 1900, 24, 105—137).—Jones' adverse criticism (*Abstr.*, 1898, ii, 640) of Morse and Burton's method (*Abstr.*, 1888, 755) of estimating boric acid is valueless, since it is based on experiments made with aqueous, instead of strongly alcoholic, solutions; trustworthy results can be obtained by adhering to the original directions. Contrary to Jones' statement, boric acid is not lost by volatilisation as ethyl borate, when, following the method, the alcoholic liquid containing the insoluble metaborate and excess of barium hydroxide is treated with an excess of carbon dioxide, and then distilled in an atmosphere of the gas; under Jones' conditions, using aqueous solutions, there is also no loss.

In order to obtain satisfactory results with the method, care has to be exercised in heating the mixture of barium borate and carbonate, as, when dried at 100° , it contains no small quantity of water; on drying for about 50 hours at 175° , or, more rapidly, at just below a red heat, it is rendered anhydrous; but on exposure to the air it rapidly absorbs water. At a full red heat the metaborate attacks the carbonate with evolution of carbon dioxide; if from this cause the weight of the mixture is too small, the necessary correction can be made by absorption of carbon dioxide from the air and subsequent drying in a desiccator, or at 500° . When once completely dehydrated, the mixture is comparatively indifferent to atmospheric moisture.

W. A. D.

Cement Testing. By O. H. KLEIN and STEPHEN F. PECKHAM (*J. Soc. Chem. Ind.*, 1900, 19, 644—645).—The authors recommend that the sample should be analysed in the same condition as received, and not dried beforehand, either at a low or high temperature; also that any insoluble matter not volatilised by treatment with hydrofluoric acid should not be called silica, although a small amount may be disregarded (compare Shimer, *Abstr.*, 1899, ii, 520).

L. DE K.

Diphenylcarbazide as a Sensitive Reagent for Metals. By PAUL CAZENEUVE (*Compt. rend.*, 1900, 131, 346—347).—The coloured products formed when diphenylcarbazide is oxidised by metallic salts (this vol., i, 465) furnish very sensitive reactions for the detection of metals, and especially of copper, mercury, and iron. A cold saturated solution of the carbazide in benzene is agitated with the aqueous solution of the salt, or, if the latter solution is not too dilute, an alcoholic solution of the carbazide may be used. Cupric salts yield a violet compound, which dissolves in benzene, and is not affected by agitation with potassium ferrocyanide solution; mercuric salts give a dull blue compound; ferric salts form a peach-flower coloration, which becomes brown if the liquid is agitated with potassium ferrocyanide solution. The reaction will detect 1 part of the metals in 100,000 of solution, and is not given by other metals. The colorations are destroyed by inorganic acids, and by excess of organic acids. Solutions of silver and gold salts yield rose colorations with precipitation of the metal.

If a solution of chromic acid, or a chromate containing 1 part in 1,000,000, or even less, is acidified with dilute hydrochloric acid and mixed with an excess of solid diphenylcarbazide, a splendid violet coloration is developed, stable in presence of inorganic acids, and quite distinct from the reactions already described. No other metal behaves in the same way. The coloured product is not removed from water by benzene, but dissolves in amyl alcohol.

C. H. B.

Action of Sodium Thiosulphate on Mercuric Salts. By FR. FAKTOR (*Chem. Centr.*, 1900, i, 1246; from *Pharm. Post*, 1900, 33, 253—254).—Aqueous solutions of mercuric salts are precipitated at the boiling point by sodium thiosulphate, with formation of mercuric sulphide. One mol. of sodium thiosulphate corresponds with 1 mol. of mercuric chloride. The process may also be applied to mercurous salts.

L. DE K.

Effect of Oxidising Agents on the Reduction of Mercuric Chloride by Oxalic Acid. By J. H. KASTLE and W. A. BEATTY (*Amer. Chem. J.*, 1900, 24, 182—188).—The reduction, in direct sunlight, of mercuric chloride by ammonium oxalate in aqueous solution is greatly accelerated by the presence of a trace of potassium permanganate. Ferric chloride and most other oxidising agents also accelerate the action, but a few, such as chromic acid and potassium chromate or dichromate, retard it. The same substances have a similar accelerating action on the reduction of thallic chloride by ammonium oxalate. The explanation given is that probably the oxidising substance used is reduced by the ammonium oxalate, and

then oxidised again by the mercuric or thallic chloride, thus acting as a "carrier" of oxygen from the oxalate to the chloride.

W. A. D.

Volumetric Estimation of Mercuric Chloride. By ERWIN RUPP (*Arch. Pharm.*, 1900, 238, 298—301).—Twenty c.c. of a solution of mercuric chloride containing about 4 grams per 100 c.c. are shaken for an hour with a little pulverised iron. The liquid is filtered and 10 c.c. are titrated with standard potassium permanganate after adding 5 c.c. of dilute sulphuric acid and 5 c.c. of a 10 per cent. solution of manganous sulphate. One mol. of ferrous chloride represents 1 mol. of mercuric chloride.

If the substance to be tested contains besides mercuric chloride any oxidisable matters or coal-tar colouring matters, potassium permanganate is added in slight excess, and this in turn destroyed by cautious addition of tartaric acid. The resulting ferric chloride is then estimated in the usual way by means of potassium iodide and sodium thiosulphate.

L. DE K.

Composition and Estimation of Cerium Oxalate. By FREDERICK B. POWER and FRANK SHEDDEN (*J. Soc. Chem. Ind.*, 1900, 19, 636—642).—Cerium oxalate has the composition $\text{Ce}_2(\text{C}_2\text{O}_4)_3 \cdot 10\text{H}_2\text{O}$. Commercial cerium oxalate is frequently contaminated with the oxalates of lanthanum and didymium. The former may be recognised by the reddish-brown colour, and the latter by the alkaline reaction of the ash, provided that no other alkaline matters are present. On the other hand, traces of cerium may be detected in the presence of lanthanum and didymium oxalates by heating 0.1 gram of the mixture with 0.5 c.c. of sulphuric acid until all effervescence ceases. The solution is then diluted with 10 c.c. of water, and after adding 1 gram of ammonium persulphate, it is again boiled, a bright yellow colour being developed if cerium is present even in traces (compare von Knorre, *Abstr.*, 1898, ii, 311).

L. DE K.

Colorimetric Estimation of Nickel in Steel. By RUDOLF FIEBER (*Chem. Zeit.*, 1900, 24, 393—394).—A series of standard samples of nickel steel in which the nickel varies from 1 per cent. upwards with a difference of about 1 per cent. between each sample are selected, and of each a solution is made as follows: 6 grams are dissolved in nitric acid, the solution is evaporated to the smallest possible volume, and rinsed into a 200 c.c. flask. The iron is then precipitated with ammonia, and when cold, the liquid is diluted to the mark; after thoroughly shaking, it is filtered and kept in a 200 c.c. flask for future use. Six grams of the sample to be examined are now treated in the same way, and the resulting filtrate is compared as regards its colour with the stock solutions. Should it not correspond with any of these, the one lighter in colour is selected as standard, and the sample is diluted with water until it shows the same colour. The percentage of nickel is then found by a simple calculation. The results are sufficiently accurate for technical purposes. The presence of chromium somewhat interferes with the test.

L. DE K.

Analysis of Titaniferous Iron Ores. By CHARLES BASKERVILLE (*J. Soc. Chem. Ind.*, 1900, 19, 419—420).—Silica is estimated in the usual manner after fusing 1 gram of the ore with 5 grams of sodium carbonate and 1 gram of potassium nitrate. After weighing the crude silica, it is heated with hydrofluoric and sulphuric acids and then reignited; the loss in weight represents pure silica.

Sulphur and phosphorus are estimated by fusing 2 grams of the ore with 20 grams of the above fusion mixture, using 'gasolene' as a source of heat. The fused mass is then extracted with water, and to the filtrate are added 25 c.c. of ferric chloride containing 0.1 gram of metallic iron. Slight excess of hydrochloric acid is added, the liquid boiled, reprecipitated with ammonia, and the sulphuric acid estimated in the filtrate. The phosphoric acid is contained in the iron precipitate, and may be estimated by the molybdate process (*Abstr.*, 1894, ii, 253).

Titanium is estimated by fusing 0.5 gram of the ore with 0.5 gram of sodium fluoride and 5 grams of potassium hydrogen sulphate for 15 minutes. The fused mass is dissolved in boiling water containing 3 c.c. of nitric acid, ammonia is added, and the excess expelled by boiling. The well-washed precipitate is dissolved in dilute hydrochloric acid, and dilute ammonia is added until a slight permanent precipitate is obtained, which is then redissolved in a drop or two of dilute hydrochloric acid (1:100). The titanium is now precipitated as usual by saturating the liquid with sulphur dioxide and boiling for a few minutes; it is then collected, ignited, and weighed as dioxide. When many assays have to be made, Weller's colorimetric process (*Abstr.*, 1883, 381) is preferable. 0.5 gram of the ore is fused with sodium fluoride and potassium hydrogen sulphate as directed, care being taken to completely expel the fluorine; the fused mass is dissolved in water containing 10 per cent. of sulphuric acid, and finally made up to 500 c.c. One hundred c.c. of the filtrate are then mixed with 5 c.c. of hydrogen peroxide, and the colour thus produced is compared with that of a series of ferruginous solutions to which a varying amount of titanium and 5 c.c. of hydrogen peroxide have been added.

Iron is estimated by the dichromate method in the filtrate from the silica.

L. DE K.

Estimation of Benzene and Ethylene in Coal-gas. By FRITZ HABER (*Chem. Centr.*, 1900, 1, 1309—1310; from *Journ. f. Gasbel.*, 43, 347—350).—The author has made further experiments with the process recommended by himself and Oechelhäuser (*Abstr.*, 1897, ii, 128) and has found it to be trustworthy.

L. DE K.

Estimation of Reducing Sugar by Means of a Centrifuge. By PH. CHAPPELLE (*Chem. Centr.*, 1900, i, 1108; from *Ann. Chim. anal. appl.*, 1900 5, 140—145. Compare this vol., ii, 112).—In the presence of several reducing sugars, the total cuprous oxide obtained is not the theoretical quantity. The cuprous oxide corresponding with a single sugar is determined by means of a factor K = cuprous oxide/sugar, which depends on the nature of the sugar and the amount of precipitated cuprous oxide. A table is given for the value

of *K* for 20 to 250 milligrams of cuprous oxide, and for dextrose, invert sugar, and lactose. An example is given showing the estimation of two of these sugars in the presence of each other; the author has not yet succeeded with a mixture containing the three.

The method is also applicable when using Sachsse's alkaline mercuric iodide solution; the mercury should be dried below 150°. The author has somewhat altered the composition of this solution, and prepares it by dissolving 22.7 grams of mercuric iodide, 40 grams of potassium iodide, and 100 grams of sodium hydroxide in water and diluting to 1 litre, and its value for dextrose and invert sugar is given; the solution is, however, sensibly affected by sucrose. L. DE K.

Estimation of Cellulose. By CONSTANTIN COUNCLER (*Chem. Zeit.*, 1900, 24, 368—369).—A criticism of the methods for the estimation of cellulose proposed by Lange, Müller, and Schulze-Henneberg. The results obtained by the first process are far too low. The others give better results, but are so difficult of execution that they are of no practical use. The author's attempt at modifying Müller's process by subjecting the wood to a preliminary treatment with calcium hydrogen sulphite ended in failure. A good and practical process is much to be desired. L. DE K.

Estimation of Cell-wall Constituents, Hemicelluloses, and Cellulose in some Plants and Parts of Plants. By ALBERT KLEIBER (*Landw. Versuchs-Stat.*, 1900, 54, 161—213).—The methods of Lange, Hoffmeister, and F. Schulze for determining cellulose gave unsatisfactory results. Concordant, if not quite satisfactory, results were obtained by boiling the cellulose, obtained by Hoffmeister's or Schulze's method, for 2 hours with 1.25 per cent. sulphuric acid. In the case of Hoffmeister's method, the same results are usually obtained whether boiling with sulphuric acid precedes or follows treatment with chlorate.

Methods for determining the cell-wall constituents are described, in which the substance was extracted with 0.15 and 0.42 per cent aqueous potassium hydroxide. It is thought that in some cases the results obtained are too high, owing to the presence of insoluble non-nitrogenous substances which do not belong to the cell-wall; on the other hand, the cell-wall itself may be attacked. The results were always higher than obtained with the crude fibre; the crude fibre does not, therefore, include the whole of the cell-wall.

Hemicelluloses are determined by boiling the residues obtained in the estimation of cell-wall constituents with 1.25 per cent. sulphuric acid. The proteids and ash are again determined in the residue. By deducting the non-nitrogenous matter in the residue from the amount of non-nitrogenous matter present before boiling with acid, numbers are obtained representing the amount of non-nitrogenous matter dissolved. The method is, for different reasons, imperfect, but it furnishes useful results. N. H. J. M.

Simple Distinction between Glue and Dextrin or Gum Arabic. By HUGO BORNTÄGER (*Chem. Centr.*, 1900, i, 1109; from *Oesterr. Chem. Zeit.*, 1900, 3, 188—189).—The suspected product is

heated with 50 per cent. hydrofluoric acid. Glue emits at once an odour of butyric acid. On evaporating on the water-bath, a white mass is obtained which gives the usual alkaloidal reactions with phosphotungstic acid, Nessler's test, and other reagents, but has not been fully investigated by the author.

L. DE K.

Estimation of Carvone in Volatile Oils. IV. By F. W. ALDEN and F. G. EHLERT (*Pharm. Archives*, 1900, 3, 9—18).—Further investigation has been made of the influence exerted by the conditions of experiment on the error of the method previously described (this vol., ii, 117). When much resin is present in the oil, the carvoxime will not crystallise, and it is necessary to distil the oil with steam and perform the estimation with the oil that distils over. When there is resin present, but not enough to prevent crystallisation, the crystals are contaminated with it, and in consequence the result is considerably too high. Better crystals are obtained if the sodium hydrogen carbonate is used in amount exactly equivalent to the hydroxylamine hydrochloride, instead of in excess, and also if a large excess of hydroxylamine is avoided.

C. F. B.

Oxidation [of Oxalic Acid by Potassium Permanganate]. By GEORG VON GEORGEVICS and L. SPRINGER (*Monatsh.*, 1900, 21, 413—421).—When an oxalic acid solution is titrated with a solution of potassium permanganate in presence of sulphuric acid, it is always observed that the beginning of the reaction is very slow, but afterwards the permanganate is instantly decolorised. The following explanation of this is suggested. The first few drops of the permanganate solution are slowly reduced to manganese sulphate; this at once reacts with an excess of permanganic acid, forming manganese dioxide, which is instantly reduced by oxalic acid.

R. H. P.

Mercurisalicyclic Acid and Millon's Reaction. By CARL J. LINTNER (*Zeit. angew. Chem.*, 1900, 707—711).—When mercuric salicylate is heated for some time at 110° or boiled with water, it is decomposed into salicylic acid, which either volatilises or dissolves, and a compound formerly regarded by Lajoux and Grandval (*Abstr.*, 1893, i, 642) as a basic salicylate, but now described as mercurisalicyclic acid, $(C_7H_5O_3)_2Hg = C_7H_6O_3 + C_7H_4HgO_3$. The latter is monobasic, dissolves without separation of mercury in aqueous sodium hydroxide or ammonium sulphide, and when boiled with water and sufficient sulphuric, hydrochloric, or nitric acid to obtain a clear liquid, gives, with sodium nitrite, a yellow colour which changes to red on adding mercuric nitrate solution. When testing for salicylic acid with Millon's reagent, mercurisalicyclic acid is probably formed on boiling with mercuric nitrate, and this, in contact with nitrous acid, gives a nitroso-compound soluble with a red colour in excess of mercuric nitrate.

The action of Millon's reagent is solely due to mercuric nitrate and nitric and nitrous acids; mercurous nitrate is inert. The best way of detecting salicylic acid by its aid is as follows: The solution is boiled with a few drops of a 10 per cent. solution of acid mercuric nitrate for 2 minutes, 2—3 drops of dilute sulphuric acid

are added, and then a few drops of a solution of sodium nitrite. The red colour shows immediately. Proteids may be similarly tested for.

L. DE K.

Commercially Pure Oleic Acid and Purified Oleic Acid. By HUGO DITZ (*Chem. Zeit.*, 1900, 24, 462—464).—Many samples of oleic acid contain a small percentage of an oily, slightly volatile, and unsaponifiable substance, varying in composition, and absorbing a considerable amount of iodine; the presence of this substance causes the turbidity noticed when titrating the sample in the usual way with alkali. From the author's investigation, it is probably an impurity introduced during the process of manufacture, and not gradually formed during the storage of the acid.

L. DE K.

Estimation of Tannic and Gallic Acids. By FERDINAND JEAN (*Chem. Centr.*, 1900, i, 1107—1108; from *Ann. Chim. anal. appl.*, 1900, 5, 134—140).—2·7 grams of iodine and 5—6 grams of potassium iodide are dissolved in water to a litre and the solution is standardised, first with a 0·1 per cent. solution of tannin, and then also with gallic acid. Ten c.c. of either solution are mixed with 5 c.c. of a cold saturated solution of sodium hydrogen carbonate contained in a beaker having a 50 c.c. mark. The iodine is slowly run in until a drop of the liquid strikes a blue colour on paper impregnated with dry starch; the liquid is now diluted to 50 c.c., and more iodine added until a blue spot is again formed. The solution of the iodine is of the requisite strength when 10 c.c. of the tannin requires 10—10·5, and 10 c.c. of the gallic acid 13 c.c. of iodine. A blank experiment showing the effect of the dilute alkali should also be made; this will generally amount to 0·4 c.c.

The decoction to be tested should contain about 0·1 per cent. of tannin, and 10 c.c. are titrated as described. Another portion is then treated as follows: Fifty c.c. are mixed in a 100 c.c. flask with 15 c.c. of a solution of albumin (2 grams of albumin rubbed to a thick paste with strong glycerol, and afterwards diluted with water to a litre), 20 grams of sodium chloride, and water added up to the mark. Twenty c.c. of the filtrate are then freed from albumin by adding a drop of acetic acid and boiling; the filtrate is titrated as before, allowance being made for the influence exercised by the salt and albumin as found by another blank experiment. The difference between the two titrations represents the tannin, whilst the second titration represents the gallic acid.

Tanning materials containing soluble starch are exhausted with alcohol. Sulphites may be allowed for by titrating with iodine in an acid solution.

L. DE K.

Rapid Estimation of the Iodine Number of Fats. By J. BELLIER (*Chem. Centr.*, 1900, i, 1109; from *Ann. Chim. anal. appl.*, 1900, 5, 128—131).—When dealing with fats having a somewhat varying iodine number and where consequently no need exists for an accurate estimation, the author uses the following process:

One gram of the fat is dissolved in 20 c.c. of a mixture of equal vols. of glacial acetic acid and chloroform previously saturated with mercuric chloride. After adding 10 c.c. of a 10 per cent. solution of potassium

iodide (if dissolved in acetic acid) the mixture is titrated with the iodine solution until it is permanently coloured for 5 minutes. This iodine solution is prepared as follows: 50 grams of iodine and 10.2 c.c. of bromine or 33.5 grams of iodine and 13.5 c.c. of bromine are dissolved in 950 c.c. of glacial acetic acid and the liquid is saturated with mercuric chloride. After a few days, 5 c.c. of either of the solutions (the second one acts the quicker, but gives off fumes) is titrated with sodium thiosulphate and then diluted with acetic acid to such an extent that 1 c.c. represents exactly 0.1 gram of iodine.

More accurate results may be obtained by adding a large excess of the reagent to the solution of the fat and then titrating the excess with thiosulphate. L. DE K.

Iodine and Bromine Values of Oils and Fats. By ROWLAND WILLIAMS (*J. Soc. Chem. Ind.*, 1900, 19, 300—301).—A table giving the iodine value by Wijs' solution, the calculated bromine value, the same as found by direct experiment, the bromine addition value, and the bromine substitution value of cocoanut oil, tallow, butter-fat, lard, castor oil, rape oil, two samples of cotton-seed oil, two samples of maize oil, japanese wood oil, menhaden oil, and nine samples of linseed oil.

Wijs' method gives excellent results if care is taken to add at least twice the amount of iodine likely to be absorbed. In some cases, notably with linseed oil, there are great discrepancies between the calculated and experimentally found bromine values. L. DE K.

Linseed Oil Analysis. By PARKER C. McILHINEY (*J. Soc. Chem. Ind.*, 1900, 19, 320—321).—The author recommends the determination of the sp. gr. and the bromine addition and substitution numbers (this vol., ii, 178). If unsatisfactory, a portion of the sample should be distilled in a current of steam and the distillate examined for turpentine, petroleum, &c. The volatile matter may easily be separated from the aqueous layer and measured or weighed. For the separation of turpentine and petroleum, Burton's nitric acid process is recommended (*Abstr.*, 1890, 669). The non-volatile matter is then collected and dried. Its acidity figure is taken, and if found to be very high, points to the presence of rosin, which must then be estimated by Twitchell's method (*Abstr.*, 1892, 389). Another portion is treated in the usual way for unsaponifiable matter (rosin oil, mineral oil). This and the distillation test are no doubt the most valuable and conclusive, as they allow of the actual separation of some of the adulterants. Finally, the saponification figure may prove to be of value. L. DE K.

Refractometric Butter Analysis. By ALFRED PARTHEIL and J. VON VELSEN (*Arch. Pharm.*, 1900, 238, 261—279).—The authors have redetermined the refractive index of different fatty compounds at various temperatures, using sodium light, and have calculated the temperature coefficients and molecular refractions. The following compounds were tested: triacetin, tributyrin, trilaurin, tripalmitin, tristearin and triolein. Samples of butter-fat, margarin, ground-nut

oil, olive oil, cotton-seed oil, and sesamé oil were also examined and the results are recorded.

It is shown that the refraction of butter increases with the iodine figure, but not to the extent expected with the Reichert-Meissl number; there is also no fixed relation between the latter and the temperature coefficient.

L. DE K.

Normal Refractometric Value for Butter. By A. LAM (*Chem. Zeit.*, 1900, 24, 394—395).—The limit of refraction of butter at 40° has been fixed in Germany at 44.2. The author, as the result of a large number of analyses of butters of Dutch origin and undoubted genuineness, states that for these butters the limit should be fixed at 46.

L. DE K.

Rancidity of Butter. By JOS. HANUŠ (*Zeit. Nahr.-Genussm.*, 1900, 3, 324—328).—A butter was again analysed after having been exposed for three months to the action of air and light. The iodine, Reichert-Meissl, and saponification numbers were but little affected, but the acidity had increased from 5.1 (?) to 75.2 c.c. of *N*/10 soda per 100 grams of butter fat.

The sample was melted, the fat dissolved in ether, and neutralised with sodium hydroxide, using phenolphthalein as indicator; the soaps were dissolved by shaking with water at 25°, the solution was evaporated to dryness and traces of fat removed by washing with light petroleum. After completely drying the soap, a large portion was dissolved in an Erlenmeyer flask in 150 c.c. of water, 15 c.c. of dilute sulphuric acid (1:5) were added, and the whole distilled in a current of steam until the volatile acid had completely passed over; the distillate was then titrated. The neutralised solution was evaporated, the residue dried at 100° and weighed, and the percentage of volatile acids calculated by Henriques' formula (*Abstr.*, 1899, ii, 258).

The non-volatile acids were estimated by Hehner's method and their molecular weight calculated from the saturation number. The unsaturated acids were calculated indirectly from the formula $100I/90.07$, where *I* represents the iodine number. The result was 2.10 per cent. of volatile acids with a mol. weight of 104; saturated non-volatile acids, 40.90; unsaturated non-volatile acids, 26.20; joint mol. weight, 278. From these data, the relation of the volatile and non-volatile acids in the isolated free acids is 1:32 (*a*), of the unsaturated to the saturated acids 1:1.5 (*b*), of the volatile to the unsaturated acids 1:13 (*c*), and to the saturated acids 1:20 (*d*). Assuming that fresh butter contains on an average 5.5 per cent. of volatile, 33 per cent. of unsaturated, and 53 per cent. of saturated acids, then $a' = 1:16$, $b' = 1:1.6$, $c' = 1:6$, and $d' = 1:9.6$.

The acidity of four fresh butters was taken and also the acidity of the distillates; the proportion of the latter to the former was approximately as 1:10, but after they had become rancid the proportion was about as 1:25.

These experiments show that the glycerides of both series of acids (volatile and non-volatile) are hydrolysed during the exposure of the butter, the non-volatile acids being set free sooner and in larger pro-

portion than the volatile ones. The glycerides of the saturated and unsaturated acids seem to be equally affected.

There is little doubt that the peculiar taste and odour of rancid butter is partly due to traces of aldehydes.

L. DE K.

Detection of "Saccharin" [o-Benzoisulphinate] in Articles of Food. By J. DE BRÉVANS (*Chem. Centr.*, 1900, i, 1105; from *Ann. Chim. anal. appl.*, 5, 131—133).—Truchon's process (this vol., ii, 377) when applied to some kinds of wine and beers or to infusion of liquorice gives untrustworthy results owing to the presence of tannins soluble in the ether-petroleum mixture. The following modification is proposed. The liquid is mixed with an excess of ferric chloride and then with a slight excess of calcium carbonate. The filtrate is then treated as directed. No 'saccharin' is retained by the iron precipitate and a subsequent violet colour is exclusively due to the presence of 'saccharin.'

L. DE K.

Estimation of Sugar in Diabetic Urine. By JULIUS TROEGER and W. MEINE (*Arch. Pharm.*, 1900, 238, 305—309).—The copper solution used by the authors differs from the ordinary Fehling's solution by containing 100 grams of glycerol per litre instead of Rochelle salt. Its exact strength in copper is determined by weighing this as subsulphide.

Sixty c.c. of the copper solution are heated in a porcelain basin with 5—20 c.c. of the sample of urine for 15 minutes. The liquid is made up to 100 c.c. in a measuring flask graduated at 45°, the warm liquid is shaken with a little talc to remove the suspended cuprous oxide, and then rapidly filtered. By estimating the copper as subsulphide in an aliquot part of the filtrate, the amount of copper oxide which has been reduced by the dextrose may be found.

L. DE K.

Estimation of Oxalic Acid and the Occurrence of Oxaluric Acid in Urine. By ERNST SALKOWSKI (*Zeit. physiol. Chem.*, 1900, 22, 437—460).—The author states that the usual process of estimating oxalic acid in urine by direct precipitation with calcium chloride in the presence of ammonia and free acetic acid gives results which are too low and proposes the following method.

500 c.c. of unfiltered urine are concentrated to about one-third. When cold, 20 c.c. of hydrochloric acid are added and the mixture is shaken three or more times in succession with 200 c.c. of a mixture composed of 9—10 vols. of ether and 1 vol. of alcohol. The united ether extract is passed through a dry filter and the ether recovered by distillation. The residual alcoholic liquid is poured into a deep basin, 10—15 c.c. of water are added, and the whole heated until the alcohol has evaporated and the liquid become clear. After filtering, the liquid is rendered faintly alkaline with ammonia and then again faintly acid with acetic acid; if this should produce a turbidity, the liquid must be again filtered. The oxalic acid is now precipitated by adding 2 c.c. of a 10 per cent. solution of calcium chloride and after 24 hours the calcium oxalate is collected, converted into oxide and

weighed. The same process may be applied to the estimation of oxalic acid in tissues.

It was accidentally discovered that the amount of oxalic acid is much increased by evaporating urine with hydrochloric acid to a syrupy consistence. 750 c.c. of a urine which yielded 6.1 milligrams of calcium oxide gave 10.2 milligrams when evaporated with 20 c.c. of hydrochloric acid. This increase is due to the hydrolysis of oxaluric acid by the hydrochloric acid. This oxaluric acid seems, according to the author's experiments, to exist in a pre-formed condition and to a larger extent then hitherto believed. If larger quantities of urine are evaporated, there is a danger of some of the oxalic acid being converted into oxaluric acid.

L. DE K.

A Quantitative Reaction of the Ureides and Purine Derivatives. II. By ADOLF JOLLES (*Ber.*, 1900, 33, 2119—2121. Compare this vol., ii, 454).—When oxidised with permanganate and sulphuric acid under the conditions already described, caffeine, hydroxycaffeine, theophylline, paraxanthine, and heteroxanthine yield as many mols. of methylamine as they contain methyl groups; the rest of the nitrogen is obtained as carbamide in the case of caffeine and hydroxycaffeine, as ammonia in the case of paraxanthine and heteroxanthine, and to about an equal extent as carbamide and as ammonia in the case of theophylline. In the case of heteroxanthine, when only about one-quarter the usual quantity of sulphuric acid was employed a very considerable amount of carbamide was formed.

C. F. B.

Estimation of Allantoin in Urine. By OTTO LOEWI (*Zeit. anal. Chem.*, 1900, 39, 266—267; from *Arch. exp. Path. Pharm.*, 1900, 44, 1).—The feebly acid urine is precipitated with mercurous nitrate to which some mercury is added. The filtrate is freed from mercury by hydrogen sulphide, and the latter expelled by warming. It is then treated with silver nitrate and magnesia, which precipitate the allantoin. In this precipitate, after thorough washing, the nitrogen may be estimated by Kjeldahl's process, or the precipitate may be decomposed by hydrogen sulphide and the filtrate evaporated to dryness, the dry residue extracted with hot water, the extract precipitated with mercuric nitrate, and this precipitate treated with hydrogen sulphide. The filtrate from the mercuric sulphide leaves the allantoin on evaporation.

M. J. S.

Estimation of Allantoin in Urine. By R. PODUSCHKA (*Zeit. anal. Chem.*, 1900, 39, 267; from *Arch. exp. Path. Pharm.*, 1900, 44, 59).—The urine (50—100 c.c.) is precipitated with an equal volume of lead acetate solution and filtered. An aliquot part of the filtrate is freed from lead with sodium sulphate; silver nitrate (5—10 per cent. solution) is then added in excess. A measured portion of the filtrate is treated with very dilute ammonia (2 c.c. of a 1 per cent. solution for 50 c.c. of the original urine) and 50—100 c.c. more of silver nitrate. The flocculent precipitate of silver allantoin is thoroughly washed on a suction filter and its nitrogen estimated.

M. J. S.

Detection of Bile Pigments in Urine. By OLOF HAMMARSTEN (*Zeit. anal. Chem.*, 1900, 39, 269—270; from *Skand. Arch. Physiol.*, 9, 313).—A mixture is made of 19 vols. of 25 per cent. hydrochloric acid and 1 vol. of 25 per cent. nitric acid, and allowed to remain for some hours, or until it has become yellowish; then, just before use, one part is mixed with 5 parts of 95—97 per cent. alcohol, and a little of the urine is added. One part of bilirubin in 50,000 parts of urine produces a characteristic green colour. Should other colouring matters be present, 10 c.c. of the urine are mixed with a few c.c. of barium chloride (or, in some cases, calcium chloride, followed by sufficient ammonia to produce neutrality), and the deposit, collected by a centrifugal machine, is treated with 1—2 c.c. of the reagent, and again centrifuged, when the presence of bile will produce a green solution.

M. J. S.

The Volumetric Estimation of Vegetable Alkaloids by Titration with Acids. By CARL KIPPENBERGER (*Zeit. anal. Chem.*, 1900, 39, 202—229; 290—314).—With the object of ascertaining which alkalimetric indicators are most suitable for the titration of alkaloids by standard acid, the author has submitted to titration small quantities (about 0.1 gram, in order that the conditions might be similar to those occurring in chemico-legal investigations) of the most generally occurring alkaloids, using eleven different indicators. The general method consisted in adding an excess of standard sulphuric acid to about 2 grams of the alkaloid, making up to a litre, and titrating the excess of acid in 50 c.c. by *N*/50 sodium hydroxide. With some indicators, the amount of acid consumed was much below the theoretical; with others, above; many of the indicators gave results of approximate accuracy, but the following gave the most satisfactory results: Atropine, morphine, veratrine, codeine, cocaine, nicotine, coniine, papaverine, narcotine with lacmoid; thebaine, codeine, emetine, coniine with iodoeosin; atropine with uranin (sodium fluorescein); coniine, morphine, thebaine, emetine, brucine, pelletierine with cochineal; aconitine, strychnine, and quinine with azolitmin; sparteine and quinine with hæmatoxylin. Narceine and caffeine could not be titrated with any of the indicators. Methyl- and ethyl-orange gave approximate results only with atropine, emetine, and coniine; phenolphthalein and alkannin could be used for sparteine, but for no other alkaloid, and Congo-red only for coniine. The cases where the consumption of acid falls below the theoretical amount are in general explicable by the fact that in such highly dilute solutions as those employed a considerable proportion of the alkaloid salt, as well as of the indicator, undergoes dissociation, such cases being most conspicuous when the indicator is of a feebly acid character and the alkaloid a weak base; in other cases, it would seem as if a compound of the alkaloid with the indicator were non-existent. With strongly acid indicators and feebly basic alkaloids, the amount of indicator used has considerable influence. Too large a consumption of acid was especially noticeable with the indicators methyl-orange, ethyl-orange, and Congo-red. This phenomenon does not seem to admit of any general explana-

tion; in some cases, it is clearly due to the formation of a compound of the alkaloid with the acid radicle of the indicator, which is not decomposed by dilute mineral acids, but as a similar effect is sometimes observed with indicators which contain no acid group, the cause remains obscure.

The above methods of titration have been applied to investigate the subject of the extraction of alkaloids from their aqueous solutions by shaking with organic solvents. It was formerly assumed that, with few exceptions, the alkaloids could not be removed by chloroform or ether from strongly acid aqueous solutions, but this is shown to be by no means the case. From a solution strongly acidified with hydrochloric acid, chloroform removes almost the whole of the papaverine and caffeine present, besides smaller amounts of codeine and cocaine in the form of free bases, strychnine, brucine, aconitine, veratrine, narceine, pelletierine, narcotine, and thebaine, in varying amounts, partly as base, and partly as hydrochloride, as well as small quantities of atropine and emetine. Morphine, quinine, nicotine, coniine, sparteine, hyoscyamine, daturine, and scopolamine are not extracted, or only in traces. From sulphuric acid solutions, large proportions of papaverine and caffeine are removed as free bases, and narcotine partly as base and partly as sulphate, whilst quantities varying from 5 per cent. to a trace were extracted of strychnine, brucine, aconitine, veratrine, narceine, emetine, and pelletierine. From solutions saturated with sodium chloride, narcotine and aconitine were wholly removed by chloroform, chiefly as salts, and atropine and quinine partially. Traces of strychnine and brucine could be removed by chloroform from solutions acidified with tartaric acid, and caffeine almost wholly from an oxalic acid solution.

Ether extracts from a hydrochloric acid solution only narcotine and caffeine in weighable amounts, besides traces of aconitine, narceine, and emetine, and from a sulphuric acid solution only caffeine in noteworthy quantity. It does not remove strychnine or brucine from a tartaric acid solution, but extracts much caffeine from one acidified with oxalic acid.

These results support the view that, even in strongly acidified solutions of the alkaloids, a large amount of dissociation into acid and base occurs.

The extraction of morphine, narceine, and strophanthin from alkaline (sodium carbonate) solutions by a mixture of chloroform and alcohol is greatly assisted by saturating the solutions with sodium chloride.

A scheme is given in the paper for the extraction and partial separation of the alkaloids, contained in an aqueous solution, based on the above facts.

M. J. S.

Quantitative Estimation of Alkaloids by means of Standardised Solution of Iodine. By MAX SCHOLTZ (*Arch. Pharm.*, 1900, 238, 301—304).—A controversy with Kippenberger (this vol., ii, 583) on the subject of the value of the iodometric method of titrating alkaloids. The author upholds his previous views.

L. DE K.

Chemico-toxicological Study of Coniine. By DIOSCORIDE VITALI and CESARE STROPPA (*L'Orosi*, 1900, **23**, 73—80).—A description is given of the method employed by the authors for the detection of coniine in the contents of the stomach of a victim of hemlock poisoning. Two new reactions of the alkaloid are given: (1) If to a little coniine or one of its salts there be added a few drops of a solution of 1 part of potassium permanganate in 200 of concentrated sulphuric acid and the mixture stirred with a glass rod, the original green colour of the acid permanganate is changed to violet. (2) On evaporating a small quantity of coniine to dryness with a few drops of concentrated nitric acid, the liquid becomes yellowish and leaves an orange-yellow residue having a peculiar aromatic odour. If to this a little potassium hydroxide solution be added, reddish-brown, oily drops separate, a very pronounced odour of hemlock is evolved, and the liquid assumes an orange-red tint. If this be evaporated to dryness, there is obtained a brown, almost black, deposit, soluble in concentrated sulphuric acid to a nearly colourless solution which, when diluted with water and carefully mixed with excess of ammonia, yields a yellow liquid. T. H. P.

Scheme for the Analysis of Rubber Wares. By OCTAVE CHÉNEAU (*Zeit. Nahr.-Genussm.*, 1900, **3**, 312—318).—To ascertain whether the article is of uniform quality, it is generally sufficient to take several samples and determine the sp. gr. and the amount of ash. The latter does not, of course, always represent the true amount of added mineral matter. Many samples contain excess of resinous matters which may be extracted with hot alcohol. The further analysis which may occasionally be considerably shortened is briefly as follows.

The finely divided sample is heated with dilute acetic acid containing a little sugar to decompose any lead dioxide. This treatment removes chalk, white lead, red lead, zinc oxide, alkalis, decomposes any ultramarine, and dissolves potato starch. The extracted mass is washed, dried at 105° and weighed, whilst the dissolved metals are estimated in the acetic acid solution. A portion of the extracted sample is now boiled for a few hours with normal alcoholic soda under a reflux condenser, the alcohol distilled off, and the residue thoroughly washed first with boiling water, then with water acidified with acetic acid, and finally with boiling water; the extraction may be repeated in case of any doubt. After drying at 105° the mass is reweighed, the loss in weight representing "factis," free and "factis"-combined sulphur, natural and added resinous matters, pitch, &c. Inferior, although not adulterated, samples may contain a rather large quantity of matters soluble in sodium hydroxide.

The residue is exhausted with acetone, which dissolves unsaponifiable mineral or rosin oils and asphalt. The acetone is distilled off, the residue dissolved in ether, and after evaporation of the latter, the unsaponifiable matter is dried at 100° and weighed.

The mass left after the treatment with acetone is extracted with cold nitrobenzene, which dissolves unvulcanised rubber and the remaining asphalt. When fully exhausted, the mass is boiled with water to re-

move the adhering nitrobenzene, dried, and weighed. It is then extracted with light petroleum, benzene, or chloroform to remove paraffin and any remaining non-vulcanised rubber. Three grams of the mass are now boiled under a reflux condenser with 3 c.c. of chloroform and 50 c.c. of nitrobenzene for an hour; when cold, 100 c.c. of ether are added, the undissolved matter is collected on a filter, washed with benzene, dried, and weighed. It may contain talc, kaolin, ochre, heavy spar, vermilion, lead sulphide, lead sulphate, and, more rarely, graphite, rasped leather, or cork, vegetable fibres, &c. These are then estimated by the usual methods, the vermilion preferably by the dry process.

The total sulphur is estimated in a separate portion by Henriques' process (this vol., ii, 124). By deducting the amount of sulphur contained in the mineral constituents, the free and organic-combined sulphur is obtained, and by deducting from this the sulphur present in the vulcanised rubber, the free and "factis"-combined sulphur is found. By deducting the sulphur found in the final residue from the sulphur left in the residue from the petroleum extraction, the sulphur in combination with rubber is obtained.

Carbon dioxide is estimated as follows. The finely divided sample, extracted if necessary with hot chloroform and nitrobenzene, is treated with dilute hydrochloric acid. The gas evolved is freed from hydrogen sulphide by passing it over pumice stone moistened with copper sulphate, dried over sulphuric acid, and finally absorbed in a weighed soda-lime tube.

L. DE K.

Chemistry of Tobacco. By RICHARD KISSLING (*Chem. Zeit.*, 1900, 24, 499—500. Compare Abstr., 1898, ii, 659, and 1899, ii, 821).—Seventeen kinds of tobacco were tested and the results recorded. The chief object was to isolate the various resins, some of which are soluble in light petroleum, others in ether, and the remainder in absolute alcohol.

The samples were dried over sulphuric acid, powdered and extracted with light petroleum (b. p. 35—55°) in the apparatus previously described. After evaporating the solvent, the residue was treated with a known weight of potassium hydroxide and distilled in a current of steam to remove nicotine, which was then estimated by the author's process. The alkaline liquid was neutralised with hydrofluosilicic acid, evaporated to dryness, and extracted with boiling absolute alcohol to dissolve resins, and a kind of wax which was quantitatively recovered by cooling to 0°; the resin was then obtained by evaporating the alcohol.

After being extracted with light petroleum, the samples were extracted first with ether and then with absolute alcohol. The extracts so obtained were treated in the same way as the petroleum extract. They contained no wax, but the alcoholic extract contained a large proportion of matters soluble in hot water, which were duly separated from the accompanying resin.

It appears that the nicotine is partly present as a resinate. There is, however, no strict relation between the amounts of nicotine and resins.

L. DE K.

General and Physical Chemistry.

Spectrum of Radium. By CARL RUNGE (*Ann. Phys.*, 1900, [iv], 2, 742—745. Compare Demarçay, this vol., ii, 586).—The author has made a spectroscopic investigation of a radium preparation with stronger dispersion than that employed by Demarçay (this vol., ii, 83). The wave-length determinations of the latter are not regarded as sufficiently exact for the characterisation of the new radium lines. Of the fifteen lines given by Demarçay as characteristic of radium, the author is able to confirm three, λ 4826.14; 4682.346; 3814.591; of the remaining twelve, some are not to be seen, others are probably barium lines. These three radium lines were also detected in a barium bromide preparation. They are not among the lines of the solar spectrum as measured by Rowland. J. C. P.

Electrical Conductivity of Compressed Powders. By FRANZ STREINTZ (*Monatsh.*, 1900, 21, 461—481).—Platinum black, amorphous carbon, and graphite have been investigated, all in the form of compressed cylinders. Special precautions have been taken to secure good and permanent contact of the powder and the electrodes. Compared with the values for solid platinum, the specific resistance of the compressed platinum black (sp. gr. = 11.6) is 6.5 times as great, whilst the temperature coefficient is about half as great. Cylinders of amorphous carbon alter their resistance after their exposure to low temperatures, and are some time in reaching a stable condition, and the specific resistance of this element decreases 1 per cent. for every 1° rise in temperature, facts that point to amorphous carbon being more nearly allied to electrolytic conductors. The compressed cylinders of graphite powder (sp. gr. = 3.0) have a temperature coefficient about twice as great as that of solid graphite, a result probably connected with the difference in density. In respect both of the absolute value of the specific resistance and of the temperature coefficient, graphite is much more nearly allied than amorphous carbon to the metallic conductors. J. C. P.

Gaseous Polarisation in the Lead Accumulator. By WALTHER NERNST and F. DOLEZALEK (*Zeit. Elektrochem.*, 1900, 6, 549—550).—When dilute sulphuric acid is electrolysed with platinum electrodes, the evolution of hydrogen and oxygen begins at an E.M.F. of about 1.7 volts, whereas in an accumulator (where the acid is electrolysed with lead electrodes) no gas is evolved at an E.M.F. of about 2 volts, the products formed being lead and lead peroxide until all the available lead sulphate has been decomposed, after which hydrogen and oxygen begin to be evolved at an E.M.F. of about 2.3 volts. This discrepancy is explained by the recent experiments of Caspari (this vol., ii, 7), which show that the minimum E.M.F. required for the liberation of hydrogen depends on the nature of the metal of which the electrode is made, metals which occlude hydrogen most readily requiring the smallest E.M.F. The accuracy of this explanation is confirmed by the following experiment. A platinum and a leaden dish of equal size were filled with solid lead sulphate and dilute

sulphuric acid. Into the acid in each a plate of lead peroxide dipped. The same small current was passed through both cells, the dishes forming the cathodes. In the platinum dish the E.M.F. between anode and cathode was 1.6 volts, in the leaden dish it was 1.92 volts, and after three weeks the lead sulphate in the platinum dish was found to be unaltered, whereas that in the leaden dish was almost wholly reduced to lead. T. E.

Gaseous Polarisation in the Lead Accumulator. By STRASSER and GAHL (*Zeit. Elektrochem.*, 1900, 7, 11).—The E.M.F. required to charge an accumulator depends, other things being the same, on whether the grating of the negative plate is made of hard or of soft lead. The authors find that this is due to the fact that a smaller E.M.F. is required to liberate gaseous hydrogen on a surface of antimony than on one of pure lead, the alloys of the two metals occupying intermediate positions. The E.M.F. also depends on the surface; it is smaller for spongy metal than for a smooth surface. The E.M.F. of the accumulator is not affected by the addition of antimony to the negative plate. The phenomenon is, therefore, another example of the influence of the nature of the metal forming the cathode on the E.M.F. required to liberate gaseous hydrogen on its surface (compare preceding abstract). T. E.

Potentials of Copper Electrodes in Solutions. Copper Precipitates of importance in Analysis. By CL. IMMERWAHR (*Zeit. anorg. Chem.*, 1900, 24, 269—278).—The author insists on the importance of knowing the solubility of the precipitates so often met with in analytical work, and by determination of a number of potentials calculates the copper ion concentrations in saturated solutions of these precipitates. The potentials of copper electrodes in contact with the complex ammonia and potassium cyanide solutions alter gradually, showing that the concentration of the copper ions changes. In the case of the cuprous salts, only the relative ionic concentrations could be determined. J. C. P.

Oxidation Potentials. By F. CROGINO (*Zeit. anorg. Chem.*, 1900, 24, 225—262).—Oxidising agents are divided into two classes; (1) those which give up oxygen; (2) those which take on or give up ionic charges. One of the most important influencing factors in the case of the second class is the acid concentration. It is shown on the lines of Jannasch and Ashoff's work (*Abstr.*, 1893, ii, 295), that by regulation of the acid concentration, a complete separation of combined iodine, bromine, and chlorine can be effected. An electrometric method of estimating an iodide is described. A platinum electrode is immersed in the solution to be titrated and the system is connected with a normal electrode. As standard potassium permanganate is gradually added to the iodide, the potential at the platinum electrode slowly alters until all the iodine is liberated, at which point a sudden change in the value of the potential is observed (compare Behrend, *Abstr.*, 1893, ii, 387). An attempt was made to measure a number of oxidation potentials on the lines of Bancroft's work (*Abstr.*, 1893, ii, 58), but constant values could be obtained only in cases where the concentration of the hydrogen ions remains

unchanged during the action—in particular for iodine. A platinum electrode immersed in potassium iodide solutions of different strengths, but always saturated with iodine, showed a potential π in agreement with the formula: $\log. K = \pi/0.0259 + \log. (I')^2/(I_2)$, where K is a constant, (I') the concentration of the iodine ions, and (I_2) that of the free iodine. The results were found to be independent of the acid concentration. When different quantities of iodine are dissolved in potassium iodide of given concentration, a form of concentration cell can be set up, and the application of Nernst's formula in this case shows that when the concentration of free iodine is very small, the E.M.F. of the cell should approach a limiting value; this is borne out by the experiments made.

The E.M.F. of an oxygen-air cell exhibits great variations; the maximum value obtained agrees well with that of Smale (*Abstr.*, 1894, ii, 436), but it is seven times the theoretical value. J. C. P.

The Discharge Potential of Chlorine Ions. By ERICH MÜLLER (*Zeit. Elektrochem.*, 1900, 6, 573—578, 581—583).—The discharge potential of chlorine ions in normal hydrochloric acid, against a normal hydrogen electrode, has been measured as 1.31 volts; this is also the E.M.F. of the hydrogen-chlorine gas cell. The author discusses the reasons for believing that hydrochloric acid acts as a depolariser for chlorine, and that the E.M.F. of 1.31 volts really indicates the beginning of a chemical reaction between the chlorine and the solution, and does not correspond with the liberation of free chlorine. His measurements show that in a normal solution of hydrochloric acid or of common salt, some other change begins at the anode when the P.D. between it and the solution is 2.2 volts (or about 1.9 volts measured against a normal hydrogen electrode).

Whether this change is the liberation of free chlorine is undecided, but the author considers that it is the one on which the electrolytic formation of chlorates mainly depends. T. E.

Migration Constant of Sulphuric Acid. By ARTHUR KENDRICK (*Zeit. Elektrochem.*, 1900, 7, 52).—Thermodynamics shows that the E.M.F. of a concentration cell depends (among other things) on the migration constant of the electrolyte. The author has measured the E.M.F.'s of concentration cells containing (a) hydrogen electrodes, (b) lead electrodes, and (c) lead peroxide electrodes in sulphuric acid of different concentrations. By means of these measurements and the equations mentioned, he calculates the values of n for hydrogen in sulphuric acid of various strengths. The results agree with the numbers obtained by other observers by measuring the changes of concentration at the electrodes (Hittorf's method) about as well as these numbers agree with each other. T. E.

Apparatus for Illustrating the Migration and Separation of Ions. By ERICH MÜLLER (*Zeit. Elektrochem.*, 1900, 6, 589—591).—The apparatus is designed for lecture illustration, to show the separation of equivalent quantities of the ions at the electrodes, and also the accompanying changes of concentration due to their different velocities. Blocks of wood suitably marked to represent the ions

slide horizontally past each other on wooden bars at different velocities. The different velocities are obtained by strings attached to pulleys of different size. When the blocks reach the ends of the bars they fall off in order to represent the separation of the ions from the solution. For details of construction, the figures in the original must be consulted. T. E.

Electro-synthesis of Organic Substances. By OCTAVE DONY-HÉNAULT (*Zeit. Elektrochem.*, 1900, 6, 533—543).—Reactions between non-dissociated substances and discharged ions are considered. In order that an ion shall part with its electrical charge, a certain difference of potential (the discharge potential) must exist between the electrode and the electrolyte. When the solution contains a substance capable of reacting with the discharged ion (a depolariser), the discharge potential is diminished. The discharge potential is measured by the method of Bose (*Abstr.*, 1899, ii, 348). Ethyl alcohol, acetic acid, acetone, acetaldehyde, quinol, and especially phenol, act as depolarisers for Cl and Br. Bromophenols may be prepared by the electrolysis of a solution of hydrobromic acid and phenol in acetic acid.

The oxidation of methyl and ethyl alcohols is studied more fully. The discharge potential of OH ions from 0.9 normal sulphuric acid, for example, is diminished by about 0.5 volt by the addition of about 20 per cent. of ethyl alcohol, whilst an equal quantity of acetaldehyde has practically no effect. Ethyl alcohol is therefore more readily oxidised than acetaldehyde, and by using a sufficiently small E.M.F. it should be possible to oxidise alcohol to acetaldehyde quantitatively. This is shown to be the case. With higher E.M.F.'s, and a correspondingly higher current density, ethyl hydrogen sulphate is also formed.

Formaldehyde was not obtained from methyl alcohol.

The order of activity of chemical oxidising agents is given by the E.M.F. which they develop in a so-called oxidation cell. By the use of an oxidising agent, giving a sufficiently low E.M.F., it should therefore be possible to attain the same results as those given by electrolytic oxidation. It is shown, in fact, that acetaldehyde is the only product of the oxidation of ethyl alcohol, in faintly alkaline solution, by lead dioxide or cupric oxide. T. E.

Electrolysis of Fused Salts. By FRIEDRICH QUINCKE (*Zeit. anorg. Chem.*, 1900, 24, 220—221).—The author previously (compare *Abstr.*, 1889, 458) regarded the deviations from Faraday's law, observed in the electrolysis of fused salts, as due to an insufficiently high internal resistance, and he sees a confirmation of this view in the recent work of Lorenz and Helfenstein (this vol., ii, 333 and 383). He supposes that, in the case of fused salts, a conductor of the second order may be converted into one of the first order, and points out that Lorenz and Helfenstein should have taken account of thermocurrents. J. C. P.

Electrolysis of Fused Salts. By RICHARD LORENZ (*Zeit. anorg. Chem.*, 1900, 24, 222—224).—The author criticises the views of Quincke (preceding abstract), and considers that the work of Lorenz and Helfenstein renders them untenable. J. C. P.

Evolution of Oxygen at the Anode in the Electrolysis of Solutions of Alkali Chlorides. By FRITZ FOERSTER and H. SONNEBORN (*Zeit. Elektrochem.*, 1900, 6, 598—604).—Neutral solutions of potassium chloride were electrolysed in such a way that the concentration at the anode remained practically constant, and that not a trace of the potassium hydroxide formed at the cathode could get into the anode solution. The concentrations of the solutions varied from 0.3 to 3.16 normal. Oxygen was evolved in all cases, and hydrogen chloride formed at the anode. Traces of chlorate were probably formed in the more dilute solutions. The quantity of hydrogen chloride formed corresponded with the quantity of oxygen liberated. This quantity decreased as the concentration of the solutions increased, 6.3 per cent. of the current producing oxygen from the most dilute solution and only 0.09 per cent. from the most concentrated. These results are very similar to those obtained with hydrochloric acid. The authors conclude that, in the electrolysis of neutral solutions of alkali chlorides, the anions of water are discharged to some extent at the anode, but that, in not too dilute solutions, the formation of chlorate and the simultaneous evolution of oxygen are almost exclusively due to the hypochlorite which is first formed by the electrolysis. T. E.

Conductivity Temperature Coefficient of some Liquid Ammonia Solutions. By EDWARD C. FRANKLIN and CHARLES A. KRAUS (*Amer. Chem. J.*, 1900, 24, 83—93).—Arrhenius (Abstr., 1889, 1044) has shown that the conductivity of solutions at first increases with rising temperature, reaching a maximum value; in the case of aqueous solutions, however, the temperatures of maximum molecular conductivity generally lie too high for experimental verification. The authors, in a preliminary investigation, find that solutions of several electrolytes in liquid ammonia pass through well-marked maxima of conductivity with rising temperature. Solutions in liquid ammonia retain the power of carrying the electric current up to and beyond the critical temperature of the solution. When potassium, sodium, and lithium are dissolved in liquid ammonia, the solutions have positive temperature coefficients of conductivity. Methylamine is found to be an electrolytic solvent. J. C. P.

Propagation of Condensation Waves in Heated Gases. By HENRI LE CHATELIER (*Compt. rend.*, 1900, 131, 30—35).—The velocity of high condensation waves in gases at the ordinary temperature has been shown to be considerably greater than that of sound, a result in accord with theory. The author's experiments show that this is also the case at high temperatures, and a noticeable point is the great decrease of velocity occasioned by reflection either from the walls or from an opposing condensation wave. Thus, in a mixture of acetylene and oxygen, the velocity of 2300 was after the first reflection reduced to 1350, after crossing an opposed wave, to 1080, and after a second crossing to 980. It is also shown that, after the passage of the wave, the whole mass of gas remains in an oscillatory state. L. M. J.

Apparatus for Melting Point Determinations. By JOSEPH HOUBEN (*Chem. Zeit.*, 1900, 24, 538).—The apparatus recommended

resembles that described by Roth (Abstr., 1886, 1070), except that the bulb and inner tube are not fused together, but are ground into one another; both are provided with perforations in their necks, which are so arranged that the sulphuric acid which they contain may be in direct communication with the atmosphere or by simply turning the inner tube may be completely shut off. J. J. S.

Liquefaction of Gaseous Mixtures. By F. CAUBET (*Compt. rend.*, 1900, 131, 108—109).—The previous work (this vol., ii, 191, 390) is extended to mixtures of methyl chloride and sulphur dioxide, and the vapour pressure curves for the mixtures are given. This case differs from those previously investigated on account of the proximity of the curves of the two constituents. Retrograde condensation was not observed, but an interesting feature is the experimental verification of the points named by Duhem the points of Gibbs and Konowaloff. L. M. J.

Dissociation in Colloidal Solutions. By M. G. LEVI (*Gazzetta*, 1900, 30, ii, 64—70).—Potassium iodide is dissociated to the same degree in solutions of gelatin, agar-agar, or silicic acid, as in aqueous solution. The lowering of the freezing point by potassium iodide and chloride, and the velocity of inversion of sugar by hydrochloric acid, have the same values in pure water as in colloidal solutions. T. H. P.

Relation of the Taste of Acid Salts to their Degree of Dissociation. II. By LOUIS KAHLENBERG (*J. Physical Chem.*, 1900, 4, 533—537).—A reply to Richards (this vol., 391), in which the author contends that the former only explains why the taste for low hydrogen concentrations is more marked than would be expected, but does not give any explanation of the fact that a solution of an acid salt possesses a sour taste when the hydrogen ion concentration is far lower than that at which the sour taste disappears in solutions of acids, as for example, hydrogen chloride. Hence he still considers the explanation of the taste on the dissociation hypothesis to be unsatisfactory. L. M. J.

Solubility of a Mixture of Salts having one Common Ion. By CHARLES TOUREN (*Compt. rend.*, 1900, 131, 259—261).—An extension of the previous work (this vol., ii, 396, 530) to mixtures of potassium nitrate and carbonate. As the latter contains two potassium ions, the concentration must be doubled in constructing the curve, and it is found that only for very low concentrations of the carbonate does the curve coincide with that for mixtures of nitrate and chloride, falling below the latter very soon, and hence indicating incomplete dissociation or the formation of KCO_3 ions even at low concentrations. Mixtures of potassium nitrate and bicarbonate were also examined, but the case is complicated owing to the fact that carbon dioxide increases the solubility of the nitrate. L. M. J.

Law of Corresponding States. By DANIEL BERTHELOT (*Compt. rend.*, 1900, 131, 175—178).—The author has previously indicated a method for the calculation of the minimum volumes of compounds,

and stated that if volumes be measured from these minima and different temperature zeros employed, the law of corresponding states is valid (this vol., ii, 335). The values of these zeros and minima are given for a number of compounds, and it is shown that these lead to results in very close accord with those deduced empirically by Madame Meyer (this vol., ii, 263).

L. M. J.

Development and Propagation of an Explosive Wave. By HENRI LE CHATELIER (*Compt. rend.*, 1900, 130, 1755—1758).—The velocity of propagation of explosive waves was measured by a photographic method; in the case of mixtures of acetylene and oxygen, the velocity of propagation of the flame is at first very great (many hundreds of metres per second), and is succeeded by the explosive wave which is characterised by a still greater and uniform velocity. The initial phenomena differ in different gases, the velocity being usually much smaller, occasionally only a few metres per second. For acetylene and oxygen, the velocity of the explosion reached a maximum of 2920 metres per sec. for the mixture $C_2H_2 + O_2$, and fell to 1850 metres for the mixture $C_2H_2 + 10O_2$, which is the limiting composition for the propagation of the wave. Other mixtures were examined, and in the case of mixtures of carbon monoxide and oxygen, it was found that when the charge of fulminate, used to induce the explosion, is great, the explosive wave does not pass, owing to its velocity being smaller than that of the compression wave produced by the fulminate.

L. M. J.

Energy of some Metallic Hydroxides deduced from the Hydrolysis of their Salts. By GIACOMO CARRARA and G. B. VESPIGNANI (*Gazzetta*, 30, ii, 35—63).—A number of measurements have been made of the electrical conductivity of, and the velocity of hydrolysis of methyl acetate by, various neutral and basic salts of iron, aluminium, &c. The results show that: (1) The basic energy of hydroxides of the metals is in accord with their position in the periodic system, decreasing, for instance, in the series Mg, Cu, Zn, Cd, Al, Fe; the assumption that ferric hydroxide is a more energetic base than aluminium hydroxide is hence erroneous. (2) Basic ferric chloride in aqueous solution is hydrolysed to a considerable extent, the basic sulphate less so, and basic aluminium sulphate much less still. (3) Even in presence of a large excess of potassium hydroxide, aluminium hydroxide forms only a potassium mono-aluminate. (4) Aluminium hydroxide acts more energetically as a base than as an acid, the degree of hydrolysis of the aluminates being fourteen times that of aluminium sulphate. (5) When dissolved in excess of not too concentrated potassium hydroxide, the oxides of lead and zinc yield respectively monopotassium plumbate and dipotassium zincate.

T. H. P.

Chemical Dynamics. Dynamical Observations on the Bromination of Benzene. By LOUIS BRUNER (*Chem. Centr.*, 1900, ii, 257—258; from *Bull. Acad. Sci. Cracow*, 1900, Januar).—In order to determine the rate of formation of bromobenzene, a bulb containing bromine was broken in the calculated quantity of benzene and the tube then sealed. After a definite time, the contents of the tube were

mixed with concentrated potassium iodide solution, and the bromine used estimated by titrating the liberated iodine. The results showed that the bromination of benzene does not stop at a limit of 50 per cent., but with a continually decreasing velocity approaches the theoretical limit. After 150 days, 94.1 per cent. was found to have been brominated. The velocity is dependent only on the concentration of the bromine, and bromobenzene has no catalytic effect on the action. The velocity is increased, however, by the presence of moisture. Experiments in which an excess of benzene was used showed that the velocity constant approached only a constant mean when calculated for a bimolecular reaction. The addition of a quantity of iodine, amounting to 1 per cent. of the benzene, increased the velocity constant ten times, whilst 2 per cent. of iodine raised its value fortyfold. By the action of 60 grams of bromine on 3 equivalents of benzene containing 2 per cent. of iodine for 7 days, a yield of 85 per cent. of bromobenzene was obtained.

E. W. W.

Velocity of the Formation of Esters from Benzoyl Chloride and Aliphatic Alcohols. By LOUIS BRUNER and STANISLAW TOLLOCZKO (*Chem. Centr.*, 1900, ii, 257; from *Bull. Acad. Sci. Cracow*, 1899, 475—487).—The velocity of the formation of esters by the action of benzoyl chloride on methyl, ethyl, propyl, *isobutyl*, *isoamyl*, and *isocapryl* alcohols has been determined. A sufficiently large excess of the alcohol was used for the unimolecular reaction $\text{Ph}\cdot\text{COCl} + \text{ROH} = \text{Ph}\cdot\text{CO}_2\text{R} + \text{HCl}$ according to the formula $K = (1/A)(\log A/A - x)$, and the constants K were determined. The results are tabulated in the original paper. The velocity constants were found to decrease rapidly as the molecular weight of the alcohol increased. Since they were found to become less as the time of the reaction was prolonged, other secondary actions must also take place.

E. W. W.

Lecture Experiments for Demonstrating Fractional Distillation. By P. N. RAIKOW (*Chem. Zeit.*, 1900, 24, 645—646).—The principles of fractional distillation may be readily demonstrated to a large audience by employing liquids which burn with different flames, for example, formic acid and ethyl benzoate. The flame is first a clear blue, then gradually assumes a yellow tinge, and finally becomes perfectly luminous.

J. J. S.

System of Indexing Chemical Literature; Adopted by the Classification Division of the U.S. Patent Office. By EDWIN A. HILL (*J. Amer. Chem. Soc.*, 1900, 22, 478—494).—A discussion of a system of indexing based upon the empirical formulæ of the chemical substances.

E. G.

Inorganic Chemistry.

Some Properties of Liquid Chlorine. By A. LANGE (*Zeit. angew. Chem.*, 1900, 683—686).—The specific gravity of liquid chlorine has been determined for temperatures between -50° and $+100^{\circ}$ by the method previously employed in the case of liquid ammonia and sulphur dioxide (see Abstr., 1899, ii, 478). The results obtained agree well with those of Knietzsch (Abstr., 1891, 14). The coefficient of expansion of liquid chlorine increases slowly but regularly, and at 90° is as great as the coefficient of gaseous expansion. The coefficient of compressibility increases from 0.000225 at 37° to 0.000637 at 93° . Liquid chlorine does not attack the iron of the containing vessel, except above 90° . The author discusses also the conditions for the safe transport of liquid chlorine. J. C. P.

Extraction of Oxygen from Air by Dissolution at a Low Temperature. By GEORGES CLAUDE (*Compt. rend.*, 1900, 131, 447—450).—The author has examined the solubility of oxygen and nitrogen at low temperatures in alcohols, ethers, acetone, chloroform, petroleum, benzene, and various inorganic liquids with a view to obtain partial separation of the oxygen and nitrogen of the air. At low temperatures, the solubility of the nitrogen increases at the same rate as that of the oxygen, and hence the method seems to be of no value for practical purposes. C. H. B.

Composition of the Air at Various Altitudes. By GUSTAVUS HINRICHS (*Compt. rend.*, 1900, 131, 442—443).—Assuming that each of the components of the atmosphere forms an atmosphere independent of the other gases, and that the pressure p of each of them at the altitude H in myriametres is given by Laplace's formula, $\log. P/p = H/K$, and that for a gas of density D the constant K has the value $1.8400/D$, and further, that there is no reciprocal action, the percentage composition of the air by volume at various altitudes will be as follows:

Altitude in myriametres.	Carbon dioxide.	Oxygen.	Argon.	Nitrogen.	Hydrogen.
0	0.3	21.00	1.20	77.75	0.02
1	0.2	18.43	0.75	80.74	0.06
2	0.1	16.07	0.46	83.26	0.20
3	0.00	13.90	0.28	85.18	0.64
4	—	11.86	0.16	85.94	2.04
5	—	9.83	0.12	83.94	6.11
6	—	7.52	0.00	75.54	16.94
7	—	4.7	—	56.2	39.10
8	—	2.2	—	31.0	66.8
9	—	0.7	—	12.9	86.4
10	—	0.3	—	4.6	95.1

It is noteworthy that the proportion of nitrogen passes through a maximum at an altitude of 4 myriametres, whilst at an altitude of 10 myriametres the atmosphere will be almost pure hydrogen.

C. H. B.

Action of Iodides and Hydriodic Acid on Sulphur Dioxide. By JAKOB VOLHARD (*Bull. Soc. Chim.*, 1900, [iii], 23, 673—674).—Referring to the recent experiments of Berg (this vol., ii, 535), it is pointed out that the action of hydriodic acid on sulphur dioxide was studied by the author in 1887 (*Abstr.*, 1889, 192). The existence of an unstable compound of hydrogen iodide and sulphur dioxide, as suggested by Berg, is considered to be improbable, and the decomposition is attributed to the simultaneous occurrence of two reactions, namely, the oxidation of the hydrogen iodide by the sulphur dioxide with the formation of iodine and sulphur, and the oxidation of the sulphur dioxide by the iodine with the further deposition of sulphur and regeneration of hydrogen iodide. N. L.

Relationship between Reactivity and Concentration of Sulphuric Acid. By WILHELM VAUBEL (*J. pr. Chem.*, 1900, [ii], 62, 141—144).—A number of the reactions of sulphuric acid depend on the hydrates that are present in the solution, rather than on the degree of electrolytic dissociation. Amongst these are the green coloration with phenylrosinduline at concentrations below 95.2 per cent., the formation of hydrogen sulphide from sodium thiosulphate at concentrations above 84.1 per cent., and the series of colours produced at different concentrations in safranin solutions. T. M. L.

Allotropic Forms of Selenium. By A. P. SAUNDERS (*J. Physical Chem.*, 1900, 4, 423—513).—Besides the author's own investigations, the paper contains an extensive *résumé* of all previous work on selenium, its physical properties and behaviour. The author considers that there are only three modifications of selenium, namely, (1) the liquid, including what are known as the vitreous, amorphous, and soluble varieties; (2) the red crystalline, and (3) the black crystalline or metallic modification. Of these, the metallic form is the most stable, the red crystalline being intermediate between the other two, with probably its potential curve cutting that of the liquid variety below the point of intersection of the other two curves, that is, below 217°, the melting point of metallic selenium. Although this view explains most of the previous observations, a few are still inexplicable. The vitreous form changes to the metallic form on heating, the velocity rapidly increasing above 60°, but there is no transition point, the metallic variety being stable at all temperatures. In no case does a change to the red crystalline form take place, except in the presence of certain solvents. Although the vitreous and amorphous varieties are regarded as identical, there are slight differences in properties which must be ascribed to differences of aggregation. In the presence of various organic liquids, amorphous selenium is converted more or less speedily into one of the other forms, and the action of a large number of liquids was studied. It is noticeable that those causing change to the metallic form are generally nitrogenous compounds, especially ring compounds, with nuclear nitrogen. The red crystals have an unstable melting point below 217°. The values for the heat of transformation obtained by various observers differ greatly; it is, however, certainly sufficient to raise the mass to the melting point, and probably considerably greater than this. Specific heat and density observations are collected, and the

author's results added. The most probable density values are ; amorphous 4.26, vitreous 4.28, red crystals 4.47, metallic 4.80. The action of light on the conductivity is discussed, and the values for the various physical constants are collected.

L. M. J.

Electrolysis of Azoimide. By ALBERTO PERATONER and GIUSEPPE ODDO (*Gazzetta*, 1900, 30, ii, 95—96).—Referring to Szarvasy's work (*Trans.*, 1900, 77, 606) on this subject, the authors call attention to the paper published by them in 1895 (*Abstr.*, 1896, ii, 245), in which they show that the deviation of the ratio of the volumes of nitrogen and hydrogen from the theoretical value is due to secondary reactions occurring during the electrolysis.

T. H. P.

Production of Nitric Acid from Air by Means of the Electric Flame. By ARTHUR McDUGALL and FRED HOWLES (*Mem. Manchester Lit. and Phil. Soc.*, 1900, 44, Pt. iv, No. 13, 1—19).—The amount of nitric acid produced by means of the electric flame depends very largely on the form of the combustion chamber ; when using about 225 watts, a large horizontal stoneware pipe gave only 98 grams per 12 H.P.-hours, whilst a vertical stoneware bottle gave 180 grams, and a second vertical chamber of conical shape gave 270 grams. The yield is greatest when the current is only just sufficient to keep the flame steady, and rose from 270 to 300 grams per 12 H.P.-hours when 172 watts were used instead of 225, but fell to 180 grams when 302 watts were used. By using instead of air a mixture of 2 vols. oxygen to 1 vol. nitrogen, the yield was raised to 590 grams, whereas Lord Rayleigh obtained 440 grams in his apparatus. The yield is decreased when the air supply is heated, and, owing to the excessive heating, is very small when a low-tension discharge between carbon poles is used.

L. M. L.

[Alleged] Conversion of Phosphorus into Arsenic and into Antimony. By FRIEDRICH FITTICA (*Chem. Zeit.*, 1900, 24, 561—562).—A reply to Winkler (this vol., ii, 476). The author considers that Winkler's failures in obtaining even minute traces of arsenic are due to the fact that the directions previously given were not accurately followed. He further states that antimony is a nitrogen derivative of phosphorus, and may be obtained in small quantities, together with arsenic, by heating amorphous phosphorus with ammonium nitrate and potassium nitrite, with or without the addition of ammonium carbonate.

J. J. S.

Metaphosphates. By GEORG VON KNORRE (*Zeit. anorg. Chem.*, 1900, 24, 369—401).—The author has reinvestigated the metaphosphates, and gives an account of the work done by other authors. Sodium trimetaphosphate, when prepared according to the methods of Fleitmann and Henneburg (*Annalen*, 1848, 65, 304, and *Ann. Phys. Chem.*, 1849, 78, 233, 238, 361), or of Lindboom (*Ber.*, 1875, 8, 122), contain small quantities of sodium hydrogen pyrophosphate and hexametaphosphate, which cannot be eliminated by fractional crystallisation. A pure salt, however, can be prepared by treating the solution with excess of a solution of lead nitrate, whereby the lead salts of the admixed phosphates are precipitated, and the pure lead trimetaphos-

phate is then decomposed with sodium sulphate. Sodium trimetaphosphate is also easily obtained in a pure state by heating sodium orthophosphate with ammonium nitrate for 6 hours at 300°. The electrical conductivity of the solutions of the salt is in accordance with the presence of a tribasic acid.

When sodium ammonium phosphate is heated, the following products are obtained: at 200°, sodium hydrogen pyrophosphate; at 280°, insoluble metaphosphate, soluble metaphosphate, and pyrophosphate; at 310°, insoluble sodium metaphosphate, together with some trimetaphosphate and pyrophosphate. Sodium dihydrogen phosphate, when heated at 210° to 240°, is converted into pyrophosphate; at 280°, it is converted into insoluble metaphosphate, pyrophosphate, and trimetaphosphate. Diammonium hydrogen phosphate yields the following salts: when heated at 155°, ammonium dihydrogen phosphate; at 166°, pyrophosphate begins to be formed; at 216°, 280°, and 360°, mixtures of phosphate, trimetaphosphate, and pyrophosphate are obtained, but an insoluble ammonium metaphosphate is not formed.

Insoluble sodium metaphosphate is obtained in almost theoretical quantities by evaporating a solution of sodium nitrate with not more than 10 per cent. excess of phosphoric acid, and then heating the residue at 330°. The three modifications of insoluble sodium metaphosphate described by Tammann (Abstr., 1892, 1050) are, according to the author, identical. E. C. R.

Action of Hydrogen on the Sulphides of Arsenic. By H. PÉLABON (*Compt. rend.*, 1900, 131, 416—419).—The interaction of realgar with hydrogen at temperatures above 300° is reversible, $2\text{H}_2 + \text{As}_2\text{S}_2 \rightleftharpoons 2\text{H}_2\text{S} + \text{As}_2$. Experiments at 610°, in tubes containing 0.5 gram of realgar and about 8 c.c. of hydrogen measured under atmospheric pressure, show a limit of the action, when R , the ratio of the partial pressure of hydrogen sulphide to the total pressure in the tube on cooling, has a value 93.07. If more than 0.3 gram of realgar is used (that is, so that some remains unvolatilised at 610°), increasing the amount of arsenic gradually diminishes the value of R until a constant value 78.69 is reached. The action of hydrogen sulphide on arsenic at 610° has a limit characterised by $R = 64.90$. All these results are shown to be in accord with the theory of dissociation. W. A. D.

Permeability of Molten Silica to Hydrogen. By P. VILLARD (*Compt. rend.*, 1900, 130, 1752—1753).—If a tube of silica attached to a manometer is exhausted and then heated by a Bunsen flame, the pressure inside rises, and it was shown that this is due to the passage of hydrogen through the walls of the tube. The permeability increases considerably when the temperature is raised sufficiently to soften the silica. L. M. J.

Double Thiosulphates and Sulphites of the Alkali Metals, Silver, and Copper. By ARTHUR ROSENHEIM and SIEGFRIED STEINHÄUSER (*Zeit. anorg. Chem.*, 1900, 25, 72—103).—A large number of the numerous double compounds of the alkali thiosulphates and sulphites with silver and cuprous thiosulphates and sulphites respec-

tively, which have been described, are evidently mixtures, and of those which may be considered as chemical compounds it is not possible to determine if they are double salts or complex compounds, since most of them are very sparingly soluble and are readily decomposed in solution. The potassium and ammonium compounds have the simpler composition, and are probably double salts; the sodium compounds are mostly of a very complicated composition, and the authors consider these to be examples of the solid-solution of cuprous and silver thiosulphates and sulphites. The following are described :

Potassium compounds :

$3\text{Ag}_2\text{S}_2\text{O}_3, 5\text{K}_2\text{S}_2\text{O}_3$;
 $\text{Ag}_2\text{S}_2\text{O}_3, 3\text{K}_2\text{S}_2\text{O}_3, 2\text{H}_2\text{O}$;
 $\text{Cu}_2\text{S}_2\text{O}_3, \text{K}_2\text{S}_2\text{O}_3, 2\text{H}_2\text{O}$;
 $\text{Cu}_2\text{S}_2\text{O}_3, 2\text{K}_2\text{S}_2\text{O}_3$;
 $\text{Cu}_2\text{S}_2\text{O}_3, 2\text{K}_2\text{S}_2\text{O}_3, 2\text{H}_2\text{O}$;
 $\text{Cu}_2\text{SO}_3, \text{K}_2\text{SO}_3$ and
 $4\text{CuSO}_3, \text{Cu}_2\text{SO}_3, \text{K}_2\text{SO}_3, 16\text{H}_2\text{O}$.

Ammonium compounds :

$\text{Cu}_2\text{S}_2\text{O}_3, (\text{NH}_4)_2\text{S}_2\text{O}_3, 2\text{H}_2\text{O}$;
 $\text{Cu}_2\text{S}_2\text{O}_3, 2(\text{NH}_4)_2\text{S}_2\text{O}_3, 1\frac{1}{2}\text{H}_2\text{O}$;
 $\text{Ag}_2\text{SO}_3, 8(\text{NH}_4)_2\text{SO}_3, 12\text{H}_2\text{O}$;
 $\text{Ag}_2\text{SO}_3, 4(\text{NH}_4)_2\text{SO}_3, 4\text{NH}_4\text{HSO}_3, 16\text{H}_2\text{O}$;
 $\text{Cu}_2\text{SO}_3, 7(\text{NH}_4)_2\text{SO}_3, 4\text{H}_2\text{O}$;
 $\text{Cu}_2\text{SO}_3, 6(\text{NH}_4)_2\text{SO}_3, 4\text{H}_2\text{O}$;
 $\text{Cu}_2\text{SO}_3, (\text{NH}_4)_2\text{SO}_3$;
 $\text{Cu}_2\text{SO}_3, 2(\text{NH}_4)_2\text{SO}_3, 3\text{H}_2\text{O}$, and
 $\text{CuSO}_3, \text{Cu}_2\text{SO}_3, (\text{NH}_4)_2\text{SO}_3, 6\frac{1}{2}\text{H}_2\text{O}$.

Sodium compounds :

$\text{Ag}_2\text{S}_2\text{O}_3, \text{Na}_2\text{S}_2\text{O}_3$;
 $\text{Ag}_2\text{S}_2\text{O}_3, 2\text{Na}_2\text{S}_2\text{O}_3, 2\text{H}_2\text{O}$;
 $\text{Cu}_2\text{S}_2\text{O}_3, \text{Na}_2\text{S}_2\text{O}_3, 2\text{H}_2\text{O}$;
 $4\text{Cu}_2\text{S}_2\text{O}_3, 3\text{Na}_2\text{S}_2\text{O}_3, 6\text{H}_2\text{O}$;
 $5\text{Cu}_2\text{S}_2\text{O}_3, 4\text{Na}_2\text{S}_2\text{O}_3, 8\text{H}_2\text{O}$;
 $\text{Ag}_2\text{SO}_3, 2\text{Na}_2\text{SO}_3, 2\text{H}_2\text{O}$;
 $\text{Ag}_2\text{SO}_3, 12\text{Na}_2\text{SO}_3, 84\text{H}_2\text{O}$;
 $5\text{Cu}_2\text{SO}_3, 2\text{Na}_2\text{SO}_3, 30\text{H}_2\text{O}$, and
 $2\text{CuSO}_3, \text{Cu}_2\text{SO}_3, 2\text{Na}_2\text{SO}_3, 8\text{H}_2\text{O}$ and $6\text{H}_2\text{O}$.

E. C. R.

Double Salts of Ammonium Thiosulphate with Silver and Copper Haloids. By ARTHUR ROSENHEIM and SIEGFRIED STEINHAUSER (*Zeit. anorg. Chem.*, 1900, 25, 103—111).—Silver chloride, when dissolved in sodium or potassium thiosulphate, undergoes double decomposition with the formation of double compounds of silver thiosulphate and alkali thiosulphate; it dissolves, however, in ammonium thiosulphate with the formation of compounds containing chlorine.

The salt, $\text{AgCl}, \text{NH}_4\text{Cl}, 4(\text{NH}_4)_2\text{S}_2\text{O}_3$, obtained by saturating a solution of ammonium thiosulphate with silver chloride and concentrating in a vacuum over sulphuric acid, crystallises in lustrous, quadratic crystals [$a : c = 1 : 0.635596$], is extremely stable, can be dissolved without decomposition in cold water or ammonia, yields a small quantity of silver sulphide when boiled with water, is decomposed by dilute acids into silver chloride, silver sulphide, sulphur, hydrogen sulphide, and sulphur dioxide, and by alkaline hydroxides with formation of silver oxide and evolution of ammonia. The corresponding bromine compound, $\text{AgBr}, \text{NH}_4\text{Br}, 4(\text{NH}_4)_2\text{S}_2\text{O}_3$, is isomorphous with the preceding [$a : c = 1 : 0.62948$]. The corresponding iodine and the thiocyanogen compounds are also described. With silver cyanide and ammonium thiosulphate, beautiful, lustrous crystals are obtained, of which, however, the various preparations differ considerably in composition, although they are identical in appearance.

Cuprous chloride yields a similar compound to silver chloride. The *chlorine* compound, $\text{CuCl} \cdot \text{NH}_4\text{Cl} \cdot 4(\text{NH}_4)_2\text{S}_2\text{O}_3$ [$\alpha : c = 1 : 0.631327$], and the *bromine* compound [$\alpha : c = 1 : 0.63828$] are isomorphous with the corresponding silver compounds. The *iodine* and *thiocyanogen* compounds, and the crystals obtained from copper cyanide are similar to the silver compounds.

Apparently, only the haloid salts of the members of the first group of the periodic system are capable of forming these complex compounds, which are similar to the double salts of potassium iodide and ethyl sulphonates of the formula $\text{R}'\text{I} \cdot 4\text{EtSO}_3\text{R}'$. E. C. R.

Composition of Bottle Glasses. By KARL ZULKOWSKI (*Chem. Zeit.*, 1900, 24, 439—440).—A reply to the criticisms of Dralle (this vol., ii, 482) on the author's previous communications (*Chem. Ind.*, 1899, 22, 280; and 1900, 23, 108). E. G.

Atomic Weight of Radio-active Barium. By SKŁODOWSKA CURIE (*Compt. rend.*, 1900, 131, 382—384).—By fractionally crystallising radio-active barium chloride (this vol., ii, 81—83, 126, 254), the authoress has isolated about 2 centigrams of a substance free from barium, which she considers to be nearly pure radium chloride. Insufficient substance was obtained to determine the atomic weight of the metal, but a sample of radio-active barium chloride, which appeared from its spectrum to contain rather more radium than barium (Demarçay), gave a value 173.9 for the atomic weight of radio-active barium; the atomic weight of radium is thus much greater than 174.

It is noteworthy that radio-active barium chloride rich in radium, after being kept several days, especially in a moist atmosphere, changes in colour and appearance and evolves an odour resembling that of potassium hypochlorite; simultaneously, the radio-activity increases. W. A. D.

Boiling Points of Zinc and Cadmium. By DANIEL BERTHELOT (*Compt. rend.*, 1900, 131, 380—382).—The boiling points were determined in an atmosphere of nitrogen by means of a thermoelectric couple of platinum and platinum-iridium, special care being taken to prevent loss of heat by cooling. Carefully purified zinc boils at 920° under 760 mm. pressure; the relationship of this result to that of other observers is discussed. Pure cadmium boils at 778° under normal pressure; the values of other observers are far from concordant, Becquerel giving 746° , Carnelley 763 — 772° , and Deville and Troost 815° . W. A. D.

Trihydrated Acid Cadmium Iodide. By D. DOBROSERDOFF (*J. Russ. Phys. Chem. Soc.*, 1900, 32, 297—300).—On passing hydrogen iodide into a pasty mass of powdered cadmium iodide mixed with a saturated solution of the salt, a large quantity of the gas is absorbed, and when all the solid is dissolved and absorption of hydrogen iodide ceases, there remains a dark brown, almost black, liquid which fumes strongly in the air and has a sp. gr. about 3. At -4.7° , this liquid

slowly solidifies to a mass of almost colourless needles of the composition $\text{CdI}_2, \text{HI}, 3\text{H}_2\text{O}$, which are decomposed in the air into hydrogen iodide and cadmium iodides, but are stable in presence of the mother liquor or in an atmosphere of hydrogen iodide. T. H. P.

Trivalent Thallium. By RICHARD JOS. MEYER (*Zeit. anorg. Chem.*, 1900, 24, 321—368).—Thallium trichloride, obtained by treating the chloride suspended in water with chlorine, crystallises with $4\text{H}_2\text{O}$ when the syrupy solution is cooled in a freezing mixture. The *tetrahydrate* is very hygroscopic, melts at 45° , and solidifies at 33° . The *monohydrate* is obtained by heating the tetrahydrate at 55° , or by crystallisation from solution at the ordinary temperature. It crystallises in lustrous, six-sided tablets, reacts acid to litmus, and when heated at 100° is decomposed with evolution of chlorine. The *hydrochloride*, $\text{TlCl}_3, \text{HCl}, 3\text{H}_2\text{O}$, crystallises in slender needles, is very hygroscopic, decomposes when heated, and when neutralised with potassium hydroxide yields the salt $\text{TlCl}_3, 2\text{KCl}$. Thallium trichloride yields with ether and ethyl alcohol the crystalline salts $\text{TlCl}_3, \text{Et}_2\text{O}$ and $\text{TlCl}_3, \text{EtOH}$. The anhydrous trichloride is obtained by extracting the ether from the preceding ether compound by means of a vacuum; it crystallises in six-sided plates and melts at 24° . Thallium trichloride yields the double salts $\text{TlCl}_3, 2\text{KCl}, 2\text{H}_2\text{O}$, $\text{TlCl}_3, 3\text{KCl}, 2\text{H}_2\text{O}$, $\text{TlCl}_3, 3\text{NH}_4\text{Cl}$, and the tribromide yields $\text{TlBr}_3, \text{KBr}, 2\text{H}_2\text{O}$. These salts can be dehydrated until the sum of the water molecules and negative radicles combined with the thallium is reduced to six; any further dehydration then results in decomposition. Only two-thirds of the chlorine is precipitated when a cold aqueous solution of thallium trichloride is treated with silver nitrate.

Compounds of Thallium Trichloride with Organic Bases.—[With C. WIEGAND.]—Thallium chloride tripyridine, $\text{TlCl}_3, 3\text{C}_5\text{NH}_5$, crystallises in white needles and is the most stable of the thallium trichloride compounds towards water. The compound $\text{TlCl}_3, \text{C}_5\text{NH}_5, \text{HCl}$ crystallises in white leaflets, the compound $\text{TlCl}_3, 3\text{C}_5\text{NH}_5, 3\text{HCl}$ in large, lustrous prisms. The trianiline chloride, $\text{TlCl}_3, 3\text{NH}_2\text{Ph}, 3\text{HCl}$, crystallises in yellow leaflets; the triethylamine chloride, $\text{TlCl}_3, 3\text{EtNH}_2, 3\text{HCl}$, crystallises in hexagonal prisms and melts at 178° ; the diethylamine chloride, $\text{TlCl}_3, 2\text{Et}_2\text{NH}, 2\text{HCl}$, melts at 112° .

Thallium tribromide, $\text{TlBr}_3, \text{H}_2\text{O}$, obtained by shaking thallium bromide with bromine water and evaporating in a vacuum with repeated additions of bromine in order to prevent reduction, crystallises in slender needles and is very unstable. The salt $\text{TlBr}_3, \text{TlBr}$, obtained by evaporating a solution of the tribromide in a vacuum as long as bromine is evolved, crystallises in red leaflets and is decomposed when treated with water. The following chlorobromides are described: $\text{TlCl}_3, 2\text{TlBr}, \text{TlCl}$, $\text{TlBr}_3, 2\text{TlCl}, \text{TlBr}$, $(\text{TlCl}_3, \text{TlCl}), 2(\text{TlBr}_3, \text{TlBr})$, and $2(\text{TlCl}_3, \text{TlCl}), (\text{TlBr}_3, \text{TlBr})$.

Thallium trinitrate, $\text{Tl}(\text{NO}_3)_3, 3\text{H}_2\text{O}$, obtained by dissolving the oxide in nitric acid, crystallises in white, lustrous crystals, effloresces on exposure to the air with evolution of nitric acid, and is a strong oxidising agent. The salt, $\text{Tl}(\text{NO}_3)_3, 2\text{KNO}_3, \text{H}_2\text{O}$, separates in large, transparent crystals. E. C. R.

Amalgams. By WILHELM KERP and WILHELM BÖTTGER (*Zeit. anorg. Chem.*, 1900, **25**, 1—71. Compare Abstr., 1898, ii, 516).—I. [With H. WINTER.]—The following crystalline amalgams have been prepared and analysed, and the temperatures determined at which they are stable when dissolved in mercury. *Sodium amalgams*, at 0° to 40·5° NaHg₆, and at 40·5° to 150° NaHg₅, are obtained from solutions of sodium in mercury. *Lithium amalgam*, LiHg₅, is obtained at all temperatures up to 100°. *Potassium amalgams*, at 0° KHg₁₄, up to 71—73° KHg₁₂, at 73° to 75° KHg₁₀, is obtained, and above 75° the solid amalgam gradually alters in composition with the rise in temperature. *Rubidium amalgams*, below 0° RbHg₁₂ is stable, and above 0° the composition of the solid amalgam varies with the rise in temperature.

II. [With H. IGGENA.]—*Strontium amalgam*, below 30° SrHg₁₂ is stable, and at higher temperatures the composition varies. *Barium amalgams*, below 30° BaHg₁₃, at 30° to 100° BaHg₁₂, are obtained.

III. Definite zinc amalgams were not obtained. *Cadmium amalgam*, Cd₂Hg₇, is obtained at 0° to 44°, and above this temperature indefinite compounds.

These crystalline amalgams have properties corresponding with true chemical compounds; the composition is the same when they are prepared from supersaturated or from non-saturated solutions; they can be recrystallised from mercury without decomposition provided the temperature at which they are decomposed is not exceeded, and they possess properties which differ from those of the alkali or alkaline earth metal from which they are formed, especially in their relative high stability to the action of air and water. The amalgam NaHg₆, when treated with potassium hydroxide at the ordinary temperature, is converted into the amalgam KHg₁₂.

The authors compare these results with those obtained by Maey (Abstr., 1899, ii, 547) and Kurnakoff (this vol., ii, 277). [Compare also Guntz and Ferée, this vol., ii, 540.] E. C. R.

New Spectra of the Rare Earths. By EUGÈNE A. DEMARÇAY (*Compt. rend.*, 1900, **131**, 387—389).—The following lines were observed in the spark spectrum of the brown oxide obtained from the most soluble portions of moderately pure (*deja assez pur*) gadolinium magnesium nitrate: $\lambda = 3704\cdot3, 3703\cdot2, 3676\cdot7, 3568\cdot4, 3561\cdot7, 3540\cdot2, 3523\cdot4, 3508\cdot5$. These lines possibly belong to terbium, but since the purity of the material used was indeterminate, they are attributed provisionally to an element denoted by Γ . In some less coloured oxides, the following lines were observed, possibly belonging to the earth $Z\gamma$ of Lecoq de Boisbaudran: 4212·6, 4195·5, 4187·3, 3978·6, 3945·0, 3595·0, 3550·0, 3531·3. The element producing these lines is denoted by Δ .

In some yttrium, containing fractions intermediate in solubility between holmium and erbium, two intense lines, 3967·9 and 3930·9 were recorded, belonging to the hypothetical element " Ω ." In the spectra of the slightly basic earths, intermediate between erbium and ytterbium, the two lines 4008·2 and 3906·5 are very intense; these are attributed to an element " Θ ."

W. A. D.

Hydrates of Manganous Iodide. By P. KUZNETZOFF (*J. Russ. Phys. Chem. Soc.*, 1900, 32, 290—297. Compare Abstr., 1899, ii, 658).—On cooling a solution of manganous iodide saturated at 0°, the tetrahydrated salt first separates out, and at -5° colourless, prismatic columns of the hexahydrate are obtained; they are very deliquescent, and at -2.7° decompose into the tetrahydrate and a saturated solution of the salt. When a solution containing 63.18 per cent. of the anhydrous salt is cooled to -40° or -45°, crystals are separated, and on adding some of these to the mother liquor at a temperature of -20.5°, there is slowly deposited stout, colourless plates of the nonhydrated salt having the melting point -9.3°.

T. H. P.

Osmond and Roberts-Austen's Theory of Iron-carbon Alloys. By E. HEYN (*Chem. Centr.*, 1900, ii, 163—164; from *Stahl und Eisen*, 20, 625—636).—The paper contains a description of Roberts-Austen's methods and results.

The fact that when the iron-carbon alloy is rapidly cooled there is no separation of graphite may possibly be explained by assuming another line of solidification for the separation of a mixture of a solid solution of 1.2 per cent. carbon in iron (Fe_c) with cementite. Such a hypothesis accords well with the want of flexibility of white irons whose sections show veins of cementite containing small particles of perlite and embedded in a matrix of perlite. As the iron-carbon alloys are allowed to cool after solidifying, the curves show several well marked breaks in continuity corresponding on the one hand with the separation of ferrite from the solution of 1.2 per cent. carbon in iron (Fe_c) and on the other with the separation of carbide (cementite) and of a eutectic mixture of ferrite and cementite. These breaks are best explained by assuming the existence of three allotropic modifications of iron. The α -form exists at the ordinary temperature, whilst the γ -form is completely converted into the β -form at about 900° in the case of iron almost free from carbon. The position of these points in the curve is, however, considerably affected by a larger amount of carbon. For instance, in the case of alloys containing 0.8 per cent. of carbon, the solid solution of carbon in γ -iron (martensite) separates into α -iron (ferrite) and cementite thus forming perlite. Alloys with less than 0.35 per cent. of carbon show three breaks in the curve, the first corresponding with a separation of β -iron from the solid solution of carbide in γ -iron, the second with the conversion of β -iron into α -iron, and the third with the decomposition of the residual solid solution of carbon or carbide in γ -iron into its components, α -iron (ferrite) and cementite. The internal structure of the crystals often found in the cavities also corresponds with these secondary changes, for their section shows a mixture of ferrite and perlite formed from the solid solution of carbon in iron.

E. W. W.

Oxidation of Salts of Cobalt and of Cerium in Alkaline Solution. By ANDRE JOB (*Ann. Chim. Phys.*, 1900, [vii], 20, 205—264).—A detailed account of work already published (Abstr., 1899, ii, 51, 61, 291, 334, 486).

W. A. D.

Supposed Decomposition of Nickel Sulphate by Light. By D. DOBROSERDOFF (*J. Russ. Phys. Chem. Soc.*, 1900, 32, 300—301).—The generally accepted statement that ordinary heptahydrated nickel sulphate is decomposed by the action of light is shown by the author to be erroneous. If the crystals occupy only a small portion of the containing vessel, they lose water with the formation of the hexahydrate, whether they are exposed to light or not. On the other hand, they are not changed, even by strong light, if the surrounding air is saturated with water vapour or if the crystals are in contact with filter paper moistened with turpentine, or if they completely fill the vessel containing them. T. H. P.

The Blue Oxide of Molybdenum. By MARCEL GUICHARD (*Compt. rend.*, 1900, 131, 389—392 and 419—421. Compare this vol., ii, 597).—The blue oxide of molybdenum, when hydrated, has the composition $\text{MoO}_2 \cdot 4\text{MoO}_3 \cdot 6\text{H}_2\text{O}$, and is thus a molybdenum dimolybdate, as considered by Berzelius. It is best obtained by mixing cold, dilute hydrochloric acid solutions of molybdenum dioxide and ammonium molybdate; the hydrochloric acid should be that of sp. gr. 1.18 diluted with 9 parts of water, this bringing about complete precipitation without decomposition. Stronger acid decomposes the oxide. The product thus obtained is nearly insoluble in cold water, although that prepared by Rammelsberg's method, by precipitation at 50° , is easily soluble; an aqueous solution of the oxide is readily obtained by leaving molybdenum trioxide and metallic molybdenum in contact in water.

The oxide obtained by precipitation is a dark blue powder of sp. gr. 3.6 at 18° ; by the evaporation of its solution, it is obtained in vitreous, faceted fragments, which yet are not truly crystalline. It dissolves in water at 50° , but is insoluble in saturated solutions of ammonium, sodium and calcium chlorides, and potassium iodide and nitrate; sodium and magnesium sulphate do not alter its solubility. It dissolves in alcohol of 95° , although insoluble in most organic solvents. When heated in a vacuum or an inert gas, it loses part of its water at 100° , and the rest near a red heat, a non-homogeneous mixture of molybdenum dioxide and trioxide being formed. Hydrogen reduces it ultimately to the metal; chlorine yields the volatile oxychloride, MoO_2Cl_2 , and molybdenum trioxide. Contrary to Berzelius' statement, it slowly oxidises in the air, and at a red heat oxygen rapidly converts it into the trioxide. Gaseous hydrogen chloride at a red heat and superheated steam decompose it, giving mixed dioxide and trioxide; gaseous ammonia gives initially the same result, but at a red heat reduces the oxides to the metal. Acetic acid does not affect it; by concentrated hydrochloric acid, it is dissolved to a yellowish-red solution of molybdenum tetrachloride, but the action is a reversible one, since, on diluting with water, the blue oxide is precipitated. With sulphuric acid, a like result is obtained. W. A. D.

Fluoro-hyperuranium Compounds. By S. LORDKIPANIDZÉ (*J. Russ. Phys. Chem. Soc.*, 1900, 32, 283—287).—By the interaction of equivalent proportions of sodium fluoride and uranium oxyfluoride, UO_2F_2 , the double compound, $\text{UO}_2\text{F}_2 \cdot \text{NaF}$, is obtained, which, when dissolved in water, gives with hydrogen peroxide an intensely yellow

solution; on evaporating the latter on a water-bath at 60—70°, a yellow, granular *precipitate* is thrown down, giving on analysis the composition $\text{UO}_4 \cdot \text{NaF} \cdot 5\text{H}_2\text{O}$. Four mols. of water are lost at 100°.

The addition of excess of hydrogen peroxide to an aqueous solution of the double salt, $\text{UO}_2\text{F}_2 \cdot 3\text{KF}$, gives an intensely yellow liquid which after some time deposits a yellow, pulverulent *double compound*, $\text{K}_4\text{U}_4\text{F}_{15} \cdot 4\text{H}_2\text{O}$ or $3(\text{UO}_4\text{KF}) \cdot \text{UO}_3\text{F}_2 \cdot \text{KF} \cdot 4\text{H}_2\text{O}$. T. H. P.

Cause of the Loss in Weight of Commercial Platinum when heated under some Conditions. By ROBERT W. HALL (*J. Amer. Chem. Soc.*, 1900, 22, 494—501).—A series of experiments is described in which platinum wires enclosed in glass tubes were heated strongly by means of an electric current, various gases being passed through the tubes; it was found that the loss of weight of platinum in carbon monoxide or dioxide is zero or very little, that in hydrogen there is a very slight gain, whilst in air or oxygen the loss is rapid. Berliner (*Ann. Phys. Chem.*, 1888, [ii], 33, 287) found that when platinum which has been exposed to air is heated in a vacuum, gas is evolved and platinum deposited on the glass cylinder surrounding the metal; he also made the observation, which the present author is unable to confirm, that the behaviour of platinum in hydrogen is exactly the same, and therefore concluded that the action is purely mechanical and caused by the escaping gases. When the platinum wire is heated in air or oxygen, there is always produced on the glass tube a lustrous metallic deposit, which, as observed by Nahrwold (*Ann. Phys. Chem.*, 1887, [ii], 31, 467), is only partially soluble in aqua regia.

From the results of these experiments, it seemed probable that an oxidising gas-flame would cause a greater loss of platinum than a reducing one, and this was proved to be the case by observing the loss of weight of a platinum crucible when heated in different parts of the blow-pipe flame.

The author considers that the behaviour of platinum when heated is best explained by the hypothesis that a volatile oxide is formed, stable at high and low temperatures, but unstable at intermediate temperatures, like the platinous chloride of Troost and Hautefeuille (*Abstr.*, 1877, ii, 273). E. G.

Platinum Compounds of Hydroxylamine. By RUDOLF UHLENHUTH (*Annalen*, 1900, 312, 235—236. Compare this vol., ii, 485).—An explanatory note relative to a claim for priority by Lossen and Alexander. M. O. F.

Ruthenium and its Compounds. III. By UBALDO ANTONY and ADOLFO LUCCHESI (*Gazzetta*, 1900, 30, ii, 71—76. Compare *Abstr.*, 1899, ii, 299).—During the conversion of ruthenium sulphate into ruthenious dithionate (*loc. cit.*) by the action of sulphur dioxide, the colour of the solution changes from bright red through green and violet to azure, after which the liquid is gradually decolorised. On pouring the azure solution into alcohol, a precipitate of the same colour, consisting of *ruthenic sulphite*, $\text{Ru}_2(\text{SO}_3)_3$, is obtained. This compound, which is an intermediate product in the above conversion, is a colloidal substance and dissolves in a large quantity of water,

giving a solution from which it is completely precipitated by the addition of a salt. It can be dried at 80° without change, but when heated in a current of carbon dioxide or nitrogen, it begins to lose sulphur dioxide at 100° , and on stronger heating is completely decomposed, with formation of a brown substance. T. H. P.

Osmium. By ARTHUR ROSENHEIM (*Zeit. anorg. Chem.*, 1900, **24**, 420—424. Compare Abstr., 1899, ii, 664).—Sodium osmichloride, when boiled with concentrated sodium hydrogen sulphite, is converted into the osmisulphite, $[\text{Os}(\text{SO}_3)_6]\text{Na}_8, 8\text{H}_2\text{O}$. By the prolonged action of excess of sodium hydrogen sulphite at the ordinary temperature, the *chlorosmisulphite*, $\text{OsCl}_2(\text{SO}_3)_4\text{Na}_6, 10\text{H}_2\text{O}$, is obtained. The same salt is obtained by the action of sodium sulphite on sodium osmichloride at the ordinary temperature.

Potassium hydrogen chlorosmisulphite, $\text{OsCl}_4(\text{SO}_3)_4\text{K}_6\text{H}_2$, obtained by the prolonged action of potassium hydrogen sulphite on potassium osmichloride, crystallises in dark red, monoclinic prisms [$a:b:c = 1.7243:1:1.1729$; $\beta = 105^{\circ}44'$]. When heated with hydrochloric acid, it evolves sulphur dioxide and is converted into potassium osmichloride. E. C. R.

Mineralogical Chemistry.

Anthracite and Anthraxolite from Canada. By W. HODGSON ELLIS and WILLIAM LAWSON (*Proc. Canadian Inst.*, 1898, N.S., 1, 67—68).—A coal-like substance (anthracite) occurring as a vein in Cambrian rocks at Sudbury gave anal. I, sp. gr. 1·865. It resembles a substance (anal. II), called anthraxolite, from near Kingston.

	C.	H.	N.	S.	Ash.	O.	Total.
I.	94·92	0·52	1·04	0·31	1·52	[1·69]	100·00
II.	90·25	4·16	0·52	0·66	0·72	[3·69]	100·00

A proximate analysis of the first of these gave: moisture, 4·00; volatile matter, 1·80; fixed carbon, 90·10; ash, 4·10. L. J. S.

Salt from Lake Djouvan-Tubé. By WLADIMIR B. MARKOWNIKOFF (*J. Russ. Phys. Chem. Soc.*, 1900, 32, 307—309).—[With K. BAILINSK.]—The salt deposited on the shores of Lake Djouvan-Tubé in the Akmolink Province, has the following composition: H_2O (of crystallisation and hygroscopic), 24·30; insoluble residue, 1·90; Cl, 12·39; SO_3 , 33·23; MgO , 5·31; Al_2O_3 , 3·97; FeO , 0·97; CaO , 1·40; Na (by difference), 14·33. T. H. P.

Von-Diestite, a new Mineral. By E. CUMENGE (*Bull. Soc. franç. Min.*, 1899, 22, 25—26).—This occurs with ores of copper and auriferous pyrites in the Hamilton and Little Gerald Mines on the Sierra Blanca, Colorado. Analysis by F. C. Knight gave:

Ag.	Bi.	Te.	Au.	Pb.	S.	Insol.	Total.
40·25	16·31	34·60	4·30	2·25	0·54	0·54	98·79

L. J. S.

Lollingite from the Harz. By ROBERT SCHEIBE (*Centr. Min. Geol.*, 1900, 119—120).—A massive mineral, occurring with calcite as a vein in gabbro at Radau-thal, is proved to be cobaltiferous lollingite by analysis I. With it are small crystals, of which the angular measurements agree more closely with mispickel than with lollingite; a partial analysis of these crystals gave II:

	As.	Sb.	S.	Fe.	Co.	Ni.	Bi.
I.	70.16	0.29	1.20	23.75	4.13	0.20	trace.
II.	—	—	7.8	—	3.5	—	—

L. J. S.

Colours of Minerals. By ARNOLD NABL (*Tsch. Min. Mitth.*, 1900, 19, 273—276).—The author has suggested that the colour of amethyst may be due to ferric thiocyanate (*Abstr.*, 1899, ii, 561), but L. Wöhler and K. von Kraatz-Koschlau (*Tsch. Min. Mitth.*, 1899, 18, 449) have failed to detect the presence of sulphur. The author has repeated his experiments, and finds distinct indications of sulphur. Also by heating amethyst at 180° he obtained 0.025 per cent. of nitrogen.

L. J. S.

Analyses of Corundum and Corundum-bearing Rock. By WILLIAM L. GOODWIN (*Rept. Bureau Mines, Toronto*, 1898, 7, 238—239. Compare this vol., ii, 552).—Crystals of corundum from Eastern Ontario gave the following results on analysis. Silica is also present (0.05—0.09 per cent.), and sometimes small quantities of cerium earths.

Al ₂ O ₃ .	Fe ₂ O ₃ .	Insol.	Loss on ignition.
96.92	—	1.36	2.43
96.26	0.36	—	1.93
97.23	0.32	—	—

Analyses are also given of the corundum-bearing rock.

L. J. S.

Phosphorescent Dolomite from Elba. By GIOVANNI D'ACHIARDI (*Jahrb. Min.*, 1900, ii, Ref. 14; from *Proc. Verb. Soc. Toscana Sci. Nat.*, 1899, 11, 156—157).—This occurs as a band in crystalline limestone at Valdana near Portolongone and at Capo Calamita. It is pale yellowish with black spots of foreign material, and is very fine grained and friable; when rubbed, it is strongly phosphorescent. Analyses gave:

CaO.	MgO.	Mn ₃ O ₄ + Fe ₂ O ₃ .	Loss on ignition (H ₂ O + CO ₂).	Insol. in HCl.	Total.
29.09	22.60	0.83	46.26	0.79	99.57
29.86	21.09	1.33	46.03	1.04	99.35

L. J. S.

[**Turquoise and Phosphorochalcite.**] By THEODOR PETERSEN (*Jahrb. Min.*, 1900, ii, Ref. 31; from *Jahresber. physik. Ver. Frankfurt a. M.*, 1896—1897, 1898, 4 pp.).—Sky-blue or green turquoise occurring as veins in weathered porphyrite at Borrow Mts., New Mexico, gave analysis I, which, after deducting 4CuO, P₂O₅ and 3CaO, P₂O₅, agrees with the formula 2Al₂O₃, P₂O₅, 5H₂O. When heated, it decrepitates violently and falls to dark brown powder.

Crystalline phosphorochalcite ("ehlite"), occurring sparsely in a quartz vein in sericite-schist at Frauenstein near Wiesbaden, gave II, agreeing with the formula $5\text{CuO}, \text{P}_2\text{O}_5, 3\text{H}_2\text{O}$. No water is lost below 150° .

	P_2O_5	Al_2O_3	Fe_2O_3	CuO	CaO	$\text{MgO}, \text{K}_2\text{O}, \text{Na}_2\text{O}$	SiO_2	Loss on ignition.	Total.
I.	27.09	32.14	1.33	4.92	5.23	0.89	8.71	15.58	99.89
II.	24.16	—	—	67.08	—	—	—	9.03	100.27

L. J. S.

A Mineral of the Columbite Group. By WILLIAM L. GOODWIN and WILLET G. MILLER (*J. Fed. Canadian Mining Inst.*, 1898, 3, 151—152; and *Rept. Bureau Mines, Toronto*, 1898, 7, 234—237).—This was found embedded in the felspar of a pegmatite containing also beryl, tourmaline, &c., at Lyndoch, Renfrew Co., Ontario. Sp. gr. 5.38. Analysis gave:

$(\text{Nb}, \text{Ta})_2\text{O}_5$	SnO_2	FeO	MnO	CuO	$(\text{Ce}, \text{Di}, \text{Y})_2\text{O}_3$	Total.
75.75	0.92	11.14	10.22	0.03	2.00	100.16

L. J. S.

Fedorowite. By CARLO VIOLA and E. H. KRAUS (*Zeit. Kryst. Min.*, 1900, 33, 36—38).—The new name fedorowite was originally given to a pyroxene which, from its optical characters, should have occupied a place between ægirine-augite and ægirite (Viola, *Jahrb. Min.*, 1899, i, 121). The following analysis (mean of two), however, shows that it resembles diopside in composition. The light green crystals occur in various volcanic rocks in the province of Rome; they are strongly pleochroic, and the angle of optical extinction on b (010) is $c : \epsilon = 65-75^\circ$; $2V < 50^\circ$.

SiO_2	Al_2O_3	Fe_2O_3	FeO	CaO	MgO	Na_2O	Total.
52.36	2.42	2.24	1.94	24.57	14.53	2.29	100.35

Fedorowite is therefore now defined as a pyroxene with the composition of diopside, but with optical characters approaching those of ægirite.

L. J. S.

Pyroxene from Moravia. By A. PELIKAN (*Tsch. Min. Mitth.*, 1900, 19, 338—339).—The following analysis by R. von Zeynek proves a pyroxene from crystalline limestone at Altstadt, Moravia, to be diopside. The same material is described crystallographically in an earlier paper (*Tsch. Min. Mitth.*, 1899, 19, 106—110).

SiO_2	Al_2O_3	Fe_2O_3	FeO	CaO	MgO	Na_2O	H_2O	C.	Total.
51.76	1.65	0.35	0.69	25.78	18.35	0.86	0.51	0.52	100.47

L. J. S.

Pyroxene from Latium. By FERRUCCIO ZAMBONINI (*Zeit. Kryst. Min.*, 1900, 33, 39—56).—Detailed crystallographic descriptions are given of the black and of the green crystals of monoclinic pyroxene from the volcanic rocks near Rome. Analysis of the black crystals gave I, and of the light green II. Another light green crystal of the same tint as II contained only 4.37 per cent. FeO; green crystals which are darker in colour contain more iron,

	SiO ₂ .	TiO ₂ .	Al ₂ O ₃ .	Fe ₂ O ₃ .	FeO.	MnO.	CaO.	MgO.	Total.
I.	48·86	0·37	5·23	1·71	10·02	0·23	24·34	8·35	99·12
II.	—	—	—	0·60	5·58	—	—	—	—

There appears to be no connection between the amount of iron and the angle of optical extinction. The crystals contain enclosures of magnetite, &c.

L. J. S.

Felspar Studies. By CARLO VIOLA (*Zeit. Kryst. Min.*, 1900, 32, 305—337).—Crystallographic and optical determinations of albite are given. Analysis I is of albite, from Amelia Co., Virginia; II, of pericline from the Kramkogel, Rauris, Salzburg.

	SiO ₂ .	Al ₂ O ₃ .	CaO.	MgO.	Na ₂ O.	K ₂ O.	Total.
I.	67·75	19·96	0·51	0·10	11·06	—	99·38
II.	67·81	20·35	0·68	0·42	10·92	0·32	100·50

L. J. S.

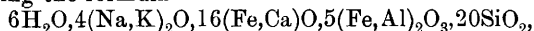
Composition of Tourmaline. By HEINRICH BEERMANN (*Jahrb. Min.*, 1900, ii, Ref. 26; from *Inaug.-Diss. Erlangen*, 1899, 37 pp. Compare this vol., ii, 602).—The following analyses of tourmaline are given. I. Black tourmaline from Epprechtstein, Fichtelgebirge; sp. gr. 3·1241. II. Rose-red tourmaline from Wolkenburg, Saxony; sp. gr. 3·106. III. Black tourmaline from Vitosa, Sofia.

	SiO ₂ .	Al ₂ O ₃ .	B ₂ O ₃ .	MnO.	CaO.	MgO.	FeO.	Na ₂ O.	K ₂ O.	Li ₂ O.	H ₂ O.	HF.	P ₂ O ₅ .
I.	36·36	32·29	9·50	—	0·46	2·60	14·32	1·39	0·66	—	1·95	—	0·06
II.	37·99	42·25	10·05	0·34	0·45	0·16	0·15	2·60	0·51	1·30	4·20	0·30	—
III.	36·29	32·18	10·14	1·50	0·42	2·04	13·13	1·41	0·40	0·08	2·40	—	—

Complicated formulæ in accordance with Rheineck's views (*Abstr.*, 1899, ii, 601) are given.

L. J. S.

Alkali-syenite from Massachusetts. By FRED. EUG. WRIGHT (*Tsch. Min. Mitth.*, 1900, 19, 308—320).—Alkali-syenite (umpteckite) occurring at Beverley, Massachusetts, consists essentially of microperthite and an alkali-hornblende, with some microcline, diopside, lepidomelane, apatite, zircon, &c. Analysis of the rock gave II; sp. gr. 2·732. The alkali-hornblende is greenish-black; sp. gr. 3·44; in its optical characters ($\epsilon : c = 20^\circ 35'$, $2E = 63^\circ 22'$, &c.) and composition, anal. I giving the formula



it is related to barkevikite, arfvedsonite, and hastingite (*Abstr.*, 1896, ii, 374).

	SiO ₂ .	TiO ₂ .	Al ₂ O ₃ .	Fe ₂ O ₃ .	FeO.	MnO.	CaO.	M ₃ O.	Na ₂ O.	K ₂ O.	H ₂ O.	Total.
I.	35·42	1·34	8·89	9·73	24·48	1·17	6·93	0·17	5·13	3·23	3·15	99·64
II.	62·99	0·16	14·25	2·78	5·15	0·18	2·72	1·30	4·86	6·35	0·18	100·92

L. J. S.

New Variety of Garnet. By W. A. MACLEOD and O. E. WHITE (*Papers and Proc. R. Soc. Tasmania*, for 1898—1899, 1900, 74—76).—A trachyte, from Port Cygnet, Tasmania, consisting of sanidine and biotite, contains numerous crystals of brownish-yellow garnet, which show trapezoidal faces and are sometimes $\frac{1}{4}$ in. diam. Analysis of the garnet gave I, and of the rock II. In the relative proportions of the bases, this differs from other garnets, and the name *johnstonotite* (after

R. M. Johnston) is proposed. [The formula, however, only approximates to the garnet formula even when all the iron is calculated as Fe_2O_3 .]

	SiO_2 .	Al_2O_3 .	FeO .	MgO .	CaO .	MnO .	Na_2O .	K_2O .	Ign.	Total.
I.	36·87	7·28	17·12	12·49	11·98	13·68	—	—	0·29	99·71
II.	55·87	18·21	8·01	0·46	4·54	2·61	3·36	5·75	2·28	101·09

L. J. S.

[Ivaarite.] By VICTOR HACKMAN (*Bull. Comm. Géol. Finlande*, 1900, No. 11, 11).—The following mineral analysis is given in a petrological paper (pp. 1—45) on the rocks associated with ijolite at Iivaara, Kola Peninsula, Finland. Ivaarite (Iiwaarit) occurs as an accessory constituent in the ijolite (a holocrystalline nepheline-pyroxene rock); the following analysis, by M. Dittrich, gives further proof of the identity of ivaarite with schorlomite.

	SiO_2 .	TiO_2 .	Al_2O_3 .	Fe_2O_3 .	FeO .	MnO .	MgO .	CaO .	Total.
	27·35	16·44	1·50	20·09	2·90	trace	0·82	30·99	100·09

L. J. S.

Meteoric Irons. By EMIL W. COHEN (*Ann. k. k. naturhist. Hofmus. Wien.*, 1900, 15, 74—94).—New analyses by J. Fahrenhorst are given of the following irons.

Salt River, Kentucky. In structure (octahedral with fine lamellæ) and composition (anal. I) this resembles the Ballinoo and Tocavita irons, (Abstr., 1898, ii, 440; 1899, ii, 307). Sp. gr. 7·6648.

Cape of Good Hope. Anal. II. Sp. gr. 7·8543. This resembles the Kokomo and Iquique irons.

Babb's Mill, Green Co., Tennessee. Analysis III and IV are of material from different portions of the mass described by Blake in 1886 under the name Green County; V is of the Babb's Mill mass described by Troost in 1845. Although these differ considerably in chemical composition, they probably represent the same fall since both belong to the rare type of ataxites rich in nickel.

	Fe.	Ni.	Co.	Cu.	Cr.	C.	S.	P.	Cl.	Total.
I.	90·89	8·70	0·85	0·04	0·00	0·02	trace	0·34	—	100·84
II.	82·87	15·67	0·95	0·03	0·04	0·03	0·00	0·09	0·01	99·69
III.	88·41	11·09	0·66	undet.	0·02	0·03	trace?	trace	0·02	100·23
IV.	88·23	11·01	0·72	undet.	0·02	0·03	trace?	trace	0·01	100·02
V.	81·45	17·30	1·67	0·03	0·03	0·07	0·01	0·12	undet.	100·68

L. J. S.

Melonite from South Australia. By ARTHUR DIESELDORFF (*Zeit. prakt. Geol.*, 1899, 423; and *Centr. Min. Geol.*, 1900, 98—100).—Melonite has recently been found in association with auriferous ores at Worturpa (this vol., ii, 283). Sp. gr. 7·403. The following analyses by G. A. Goyder are quoted from *The Chronicle*, Adelaide.

	Te.	Se.	Ni.	Co.	Fe.	Au.	SiO_2 .	Total.
	77·52	2·49	19·11	0·10	0·68	0·07	0·08	100·05
	80·46	undet.	18·12	0·03	0·68	undet.	0·74	100·03

L. J. S.

Physiological Chemistry.

Mass and Oxygen Capacity of Blood in Man. By JOHN S. HALDANE and J. LORRAIN SMITH (*J. Physiol.*, 1900, 25, 331—343).—A full account of experiments previously published (this vol., ii, 416). The main conclusions are the following: The mass of the blood in man is about 4·9 per cent. of the body weight, and varied in fourteen persons from 3·34 to 6·27. The total oxygen capacity of the blood in litres is 0·85 per cent. of the body weight in kilograms, and varied between 0·57 and 0·95. The percentage oxygen capacity is 18·5 per cent., the limits being 16·0 and 20·9. The oxygen capacity of blood, even from different animals, varies in direct proportion to its colouring power, and may be accurately determined colorimetrically by reference to blood of known oxygen capacity. W. D. H.

Absorptive Power of Hæmoglobin for Oxygen and Carbon Monoxide. By L. G. DE SAINT MARTIN (*Compt. rend.*, 1900, 131, 506—509).—One gram of hæmoglobin always absorbs the same volume of both oxygen and carbon monoxide. Although the absorptive power for the two gases is equal, it is not a fixed quantity. G. Hüfner (*du Bois Reymond's Archiv*, 1894, 130) gives, as the result of a number of observations, the number 1·34, which represents the number of c.c. of oxygen absorbed by 1 gram of hæmoglobin. In the present research, the numbers obtained in seven observations on dogs' blood are respectively 1·35, 1·22, 1·35, 1·33, 1·34, 1·20, and 1·35. The figures obtained from various pathological specimens of human blood are as follows: 1·305, 1·19, 1·33, 1·26, 1·22, 1·18, 1·26, 1·34. This variation cannot be accounted for by any change in the blood-pigment that can be detected by the spectro-photometer. W. D. H.

Agglutination of Blood Corpuscles by Chemical Agents. By E. HÉDON (*Compt. rend.*, 1900, 131, 290—292).—In solutions of non-dissociable substances, such as sugar, very weak doses of acid (mineral or organic) produce agglutination of blood-corpuscles, but in solutions of electrolytes, such as salts, this is not the case. The addition of a certain quantity of neutral salt in the former case prevents the agglutination, or, if agglutination has occurred, produces disagglutination. W. D. H.

Changes in the Composition of the Blood after Transfusion of Sodium Chloride, and their Relationship to Diuresis. By R. MAGNUS (*Chem. Centr.*, 1900, i, 1036; from *Arch. exp. Path. Pharm.*, 44, 68—103).—The experiments recorded were made on dogs. If large quantities of blood are first withdrawn, the blood drawn subsequently is more dilute; but if the first withdrawal does not exceed 8 per cent. of the total blood in the animal, the blood drawn afterwards is more concentrated; this is due to increase in the amounts of hæmoglobin and proteid; the proportion of salts is not altered. After transfusion of 0·9 per cent. solution of sodium chloride, there is

diuresis, and proportionally more sodium chloride is excreted than water. Stronger salt solutions produce less diuresis. In some cases, sugar appears in the urine. After the injection of hypotonic solutions, the osmotic pressure sinks, and remains low until the diuresis comes to an end. The capillary wall has, therefore, the power to rapidly regulate the osmotic pressure of the blood. Diuresis is a result of dilution of the blood. By the use of strong salt solutions, water enters the blood from the tissues.

W. D. H.

Functions of the Nucleus in Relation to Hæmoglobin Formation and Cellular Protection. By HENRI STASSANO (*Compt. rend.*, 1900, 131, 298—301).—In studying the absorption of iron saccharate in the peri-oesophageal membrane of the frog, it was noticed that the nuclei of the endothelial cells and of the blood-corpuscles absorb the iron. In the case of the blood-corpuscles, the chromatin of the nucleus diffuses into the cell-protoplasm in order to combine with the salt injected. The same diffusion of chromatin was noted in certain changes of environment (reaction, temperature, &c.) of the corpuscles. The nucleus is believed, therefore, to be a protective agent, as well as being concerned in the assimilation of nutriment and elaboration of hæmoglobin.

W. D. H.

Influence of Acids on the Amylolytic Action of Saliva. By G. A. HANFORD (*Amer. J. Physiol.*, 1900, 4, 250—260).—It is not possible to designate any percentage of acid or alkali which inhibits salivary digestion in a definite degree. The character of the action is dependent also on the absolute amount of the saliva and the attendant variation in the quantity of proteid matter present. Whenever free hydrochloric acid is present, more or less complete inhibition is certain to result.

W. D. H.

End Products of Gastric Digestion. By MEINHARD PFAUNDLER (*Zeit. physiol. Chem.*, 1900, 30, 90—100).—Attention has been recently directed to the question of the nature of the substances formed during peptic activity which do not give the biuret reaction. In the present research, the digestion was allowed to go on for some months, the albumoses were removed by zinc sulphate, and the peptone by iodine or by phosphotungstic acid; the last-named substance precipitates other products also. In the case of serum-albumin, the final filtrate contained 39·7 per cent. of the total nitrogen. Among the products separated out were leucine and a diamino-acid, probably histidine. In the case of fibrin, leucine was not found. The principal end products appear to be substances intermediate between peptone and the amino-acids; these do not give the biuret reaction, and contain more than one carbon nucleus; in the case of serum albumin at least, a leucine and diamino-nucleus are present.

W. D. H.

Quantitative Relationships of Pepsin Activity. By JULIUS SCHÜTZ (*Zeit. physiol. Chem.*, 1900, 30, 1—14).—E. Schütz (Abstr., 1885, 1147) stated that the amount of the products of peptic activity was proportional to the square root of the amount of pepsin. The method used was to estimate the products by their rotatory power. This statement has been but little credited. It was, however con-

firmed by Borissow (*Inaug. Diss. Petersburg, 1891*), who used Mett's capillary tube method. In the present research, various proteids were used, and the amount of digestive products was estimated by nitrogen determinations. The rule is again confirmed, and it is believed to hold for other enzymes also. One example will suffice :

Amount of solution of pepsin in c.c.	Digested nitrogen in grams.	
	Found.	Calculated.
1	0.0230	0.0223
4	0.0427	0.0446
9	0.0686	0.0669
16	0.0889	0.0892

W. D. H.

Nutritive Value of Hetero-albumose from Fibrin, and Proto-albumose from Casein. By LEON BLUM (*Zeit. physiol. Chem.*, 1900, 30, 15—44).—The experiments were performed on a dog. They show that all proteoses have not the same nutritive value, and that of the two investigated, the caseose is the more valuable. The following table illustrates this :

Food.	Nitrogen.		Balance.
	Intake.	Output.	
1a. Meat	14.12	13.81	+ 0.31
1b. Hetero-albumose ...	14.12	15.30	- 1.18
2a. Meat	14.7	14.0	+ 0.7
2b. Proto-caseose	14.7	14.4	+ 0.3

A discussion follows as to why this should be. Investigation of the substances given as food in relation to the way in which their nitrogen is combined by Hausmann's method did not yield an answer to the question.

W. D. H.

Comparative Absorption [Digestibility] and Velocity of Hydrolysis of Certain Fats. By H. LUHRIG (*Chem. Zeit.*, 1900, 24, 646—648. Compare this vol., ii, 224, 355 ; Kreiss and Wolf, *ibid.*, 324).—According to König, butter is readily digested because it is so easily hydrolysed. Comparative experiments made by the author on butter, margarine, lard, cotton-seed oil, sesamé oil, and cocoanut butter indicate that in all five cases the hydrolysis proceeds similarly and to appreciably the same extent when cold alcoholic potash of a given strength is employed. There thus appears to be no relationship between the ease with which a fat is absorbed and the readiness with which it is hydrolysed.

J. J. S.

Absorption of Coloured Fats. By EDUARD PFLÜGER (*Pflüger's Archiv*, 1900, 81, 375—380).—Hofbauer (this vol., ii, 605) has stated that fat particles are absorbed as such, for if the fat is artificially coloured, the fat droplets in the epithelial cells are still coloured. The pigments used are insoluble in water. The present research shows that although the pigments are insoluble in water they are soluble in bile, in soaps, and in glycerol. Hofbauer's work gives therefore no proof that fat is absorbed as an emulsion,

W. D. H.

Absorption of Fat. By HANS FRIEDENTHAL (*Centr. Physiol.*, 1900, 14, 258—261).—Hofbauer's work, although conclusive at first sight, really does not solve the question of fat-absorption. The absorption of fat in the large intestine where there is an absence of steapsin (Hemmeter, this vol., ii, 607) either shows that neutral fat can be absorbed as such, or that the first part of the epithelial cells is analytic, and the deeper portion synthetic in its action. The main objection to Hofbauer's method is that the pigments he used are soluble, not only in fat, but also in fatty acid. This is regarded as a more important objection than those urged by Pflüger (see preceding abstract). In fact, it is stated that alkanna is not soluble in soaps unless free fatty acid is present as well. W. D. H.

Formation of Fat in the Animal Organism by Intensive Feeding of Fat. By V. HENRIQUES and C. HANSEN (*Expt. Stat. Record*, 1900, 11, 674—676; from 44^{te} Ber. k. Vet. Landbohøjsk. Lab. Landokon. Forsøg., 1899).—Two pigs (3 months old) were fed during 168 days with ground barley and melted cocoanut, or linseed oil mixed with water. At suitable intervals a few grams of fat were taken from the backs of the animals and examined. The daily amount of oil was gradually increased from 125 to 400 grams.

The results showed that linseed oil was present in the newly-formed fat. At the conclusion of the experiments, when the animals were killed, large quantities of sativic acid (hydroxylinoleic acid) were found in the fatty tissue.

The iodine numbers for the fat of pig (1), which had cocoanut oil all the time, were: October 10, 70·3; December 12, 57·5; December 30, 71·8; February 1, 92·8, and March 17, 100·3. The refraction numbers at the same dates were 60·5, 56·9, 60·6, 64·2, and 65·4. The second pig, which had linseed oil until December 9, and afterwards cocoanut oil, gave the following results: iodine numbers, 70·9, 109·2, 88·3, 83·8, and 69·7; refraction, 60·8, 66·7, 64·2, 62·2 and 59·8.

Experiments with two cows are also described. The one had 0·5 kilo. of emulsified linseed oil in addition to hay, ground barley, and linseed meal, the other 0·5—1 kilo. of oil. During the first 4—6 days, the percentage of fat in the milk was increased in some cases by almost 1 per cent.; subsequently, however, the percentage of fat became normal, notwithstanding that feeding with oil was being continued. The yield of milk changed in the same manner as the percentage of fat in the milk.

During the feeding with oil the volatile fatty acids of the butter fat greatly decreased; the lowest Reichert numbers obtained were (cow 1) 16·5, and (cow 2) 12·5 for 5 grams of fat. The amounts of volatile fatty acids only slowly became normal after the oil-feeding was discontinued. The iodine number and index of refraction changed rapidly both with oil feeding and after it was discontinued; the highest iodine number obtained was 70·4. The melting point of the butter fat increased from 35·4° (normal food) to 39° (linseed oil, 0·5 kilo.). Sativic acid was found only in small quantities in the butter fat; there was therefore no important transfer of food fat to the milk. At the same time, the results of the Hübl test showed

that Soxhlet's theory is wrong, since the iodine number of beef fat is 40, whilst that of the butter fat obtained during the oil-feeding was about 58. Partially starved cows yield milk in which the amount of volatile fatty acids remains practically unchanged, whilst the iodine number is raised and the melting point lowered. This would seem to indicate a migration of the liquid constituents (olein) of the fatty body-tissue to the milk.

The conclusion is drawn that when much fat is supplied in the food, it is secreted as milk fat after having been transferred to the blood. The transmission is not, however, direct; in the alveolar cells of the milk gland, the fat will be transformed in such a manner that much olein and a small amount of fat having a high melting point (stearin?) are formed. Large amounts of drying oil in the food will be changed to non-drying oils before being secreted in the milk. N. H. J. M.

Origin of Volatile Fatty Acids in Butter. By NATHAN ZUNTZ and USSOW (*Chem. Centr.*, 1900, i, 1135; from *Arch. Anat. Phys. Physiol. Abth.*, 1900, 382—384).—It is well known that the fat of cow's milk is rich in lower glycerides, whilst that of human and dog's milk is not. In the expectation that this might depend on the absorption of lower fatty acids produced by fermentation from carbohydrates during digestion, a dog was fed on butter, butyric acid, and sodium butyrate, but the amount of volatile fatty acid did not rise in the milk. It therefore appears that in the cow these volatile acids are actually formed in the mammary glands. W. D. H.

Mineral Metabolism in the Naturally and Artificially Fed Infant. By MAGNUS BLAUBERG (*Zeit. Biol.*, 1900, 40, 1—35, 36—53).—The mineral metabolism in infants is important in view of such diseases as rickets. Observations are here recorded on four children, each fed in a different way; the inorganic constituents of urine and faeces were examined in detail. In one fed on diluted cow's milk, 53.72 per cent. of the saline constituents were absorbed, and the remainder passed away in the faeces. Of the individual salts, the sodium compounds were absorbed best (87 per cent.); the numbers for potassium salts, chlorides, phosphates, and calcium oxide were respectively 67.6, 59.3, 46.6, and 37.25. There is a loss of iron. The proportion is seen to be different from that required by the needs of the organism. The results compare unfavourably with those obtained in another child fed on human milk. The results are still more unfavourable if Kufeke's meal and water are used instead of milk. Here the balance is often on the wrong side (salt-hunger). If undiluted cow's milk is employed, a condition of over-nutrition is noted. W. D. H.

Proteid-Metabolism during Gelatin-Feeding. By JOSEPH KIRCHMANN (*Zeit. Biol.*, 1900, 40, 54—94).—Experiments were performed on a dog to determine to what degree gelatin acts as a proteid-sparing food. The gelatin was practically all absorbed; traces only were found in the faeces. If gelatin in amount corresponding with 12 per cent. of the necessary energy is given, proteid decomposition is lessened by 27 per cent. Increase of the administered gelatin

beyond this lessens proteid katabolism in a proportionally small degree, thus gelatin to the extent of 62 per cent. lessens the proteid decomposition by 35 per cent. This was the maximum obtained. A discussion of the results of previous workers is added. W. D. H.

Influence of Sodium Chloride Solution Injected Subcutaneously on Proteid Metabolism. By OTTO KRUMMACHER (*Zeit. Biol.*, 1900, 40, 173—179).—The question what influence physiological salt solution has on metabolism is important, because it is so frequently used as a vehicle for other substances. Biernacki (*Zeit. Klin. Med., Suppl.* 19, 49—86) states that after injecting 100 to 300 c.c. of a 0.7 per cent. solution of sodium chloride in dogs proteid katabolism is increased by 70 per cent. His methods are criticised, and a repetition of his experiments shows that the increase is very small. Before the injection, the excretion of nitrogen averaged 2.56 grams daily; this was raised to 2.75 by the injection of 210 c.c. of the saline solution. The amount of sodium chloride in the urine was increased.

W. D. H.

Influence of Sodium Salicylate on Metabolism. By FRANCIS W. GOODBODY (*J. Physiol.*, 1900, 25, 399—413).—Sodium salicylate in man causes increased katabolism of proteid material; this leads to an increase of nitrogen, particularly in the form of urea, which is excreted. It does not influence general metabolism, or absorption of fats or proteids.

W. D. H.

Rôle of Arsenic in Connection with the Menstrual Flow. By ARMAND GAUTIER (*Compt. rend.*, 1900, 131, 361—367).—Administration of arsenic improves the skin and its appendages, and lessens the intervals between the menstrual epochs. Much the same is true for iodine. The thyroid is of all the organs the richest in these two elements. Arsenic is absent in healthy blood, except during menstruation, when 0.28 milligram per kilogram of blood are present. Iodine also increases in the menstrual blood. The fall of hair, and epithelial desquamation are in man considered sufficient to balance the arsenic and iodine metabolism of the thyroid. In woman, the balance is assisted by the menstrual flow. Examples are quoted from man and animals to emphasise the inter-relationships of the functions of skin, thyroid, and genital organs.

W. D. H.

Metabolism of Iodine. By PAUL BOURCET (*Compt. rend.*, 1900, 131, 392—394).—Iodine does not exist merely in the thyroid and the blood, but in smaller quantities in most of the tissues and organs. Analytical figures in dog and rabbit are given. A man takes in his food about 0.33 milligram of iodine daily. It is eliminated principally by the epidermis and skin glands; the hair and nails are particularly rich in this element. They contain also about the same quantity of bromine. In woman, where the fall of hair is not such a marked occurrence, the excess is carried off in the menstrual discharge.

W. D. H.

Glycogen Formation after Inulin Feeding. By R. NAKASEKO (*Amer. J. Physiol.*, 1900, 4, 246—250).—The experiments show that

the glycogen-forming properties of inulin in the case of the rabbit are uncertain or minimal. W. D. H.

Formation of Lactose. By BENJAMIN MOORE and WILLIAM H. PARKER (*Amer. J. Physiol.*, 1900, 4, 239—242).—It has been generally assumed that the mammary glands form, and not merely excrete, lactose, and that this substance when found in the urine arises from absorption from the charged gland cells, but this hypothesis does not appear to have been experimentally demonstrated. The present experiments on goats show that it is well founded. The mammary glands were removed; parturition occurred, but the urine remained practically normal; certainly no lactose was found in it.

W. D. H.

Connective Tissue in Muscle. By J. H. GOODMAN (*Amer. J. Physiol.*, 1900, 4, 260—263).—The connective tissue can be separated from muscle by a simple mechanical process first described by E. Schepilewsky (*Arch. Hyg.*, 1899, 34, 348), and among its constituents this observer describes a mucin. It is here shown, however, that the substance precipitated by acetic acid yields no reducing substance, and contains as much as 16 per cent. of nitrogen; it is therefore not mucin, neither is it a nucleo-proteid. The gelatin obtained gives Millon's reaction; the old statement that gelatin does not give this reaction is incorrect.

W. D. H.

Chemistry of the Brain. By N. ALBERTO BARBIERI (*Compt. rend.*, 1900, 131, 347—349).—When brain matter was kept at 45° for 12—18 hours, carbon dioxide came off to the amount of about 1 c.c. for each gram of brain taken. The residue, on distillation, yields a small quantity of alcohol. The other substances separated are loosely described as (1) the hydrochloride of a ptomaine, (2) a substance of phenolic nature, (3) a crystalline material intermediate between leucine and butalanine, (4) cholesterol, margarine, stearin, olein, (5) a substance with a fishy odour, and (6) a residue which probably consists largely of keratin.

W. D. H.

Thyroid Gland of Sheep. By TH. SUIFFET (*J. Pharm.*, 1900, [vi], 12, 50—53).—With sheep grazed on inland pastures the amount of iodine in the thyroid gland varies from 0.0735 to 0.088 per cent., whilst with sheep from pastures near the sea or near salt marshes it varies from 0.121 to 0.140. It is probable that the high percentage of iodine in the latter case is due to the presence of *Salicornia*, *Salsola soda*, and *Atriplex portulacoides* in the pasturage; an analysis of the ash of these plants, however, will be necessary to confirm this view.

W. A. D.

Fermentative Decomposition of Proteid, and Ammonia Formation in the Liver. By MARTIN JACOBY (*Zeit. physiol. Chem.*, 1900, 30, 149—173).—Changes in the Liver during Phosphorus Poisoning, and their Relation to Autolysis (*ibid.*, 174—181).—Loewi (Abstr., 1898, ii, 617) has stated that by the action of liver ferment solutions on glycine, a substance soluble in ether or

alcohol is obtained which is not urea, but contains easily detachable nitrogen. The present investigation was originally undertaken to determine what this substance is, but resulted in the discovery of an ammonia-forming enzyme in the liver. A number of experiments were performed in which glycine was added to liver juice, in order to see if any increase in the nitrogen which can be driven off by magnesia took place; this was not found. In liver juice preserved by the addition of toluene, it was, however, observed that without any further addition, and in the absence of putrefaction, the amount of this loosely combined nitrogen rose considerably; in one experiment, in which a sample of the aqueous liver extract was examined daily, the amount of this nitrogen rose gradually in 20 days from 0.0013 gram to 0.00675 per 20 c.c. This does not occur when the extract is boiled and then kept. The nitrogen is found to correspond in amount mainly with the quantity of ammonia newly formed, and this arises from an increase of amino-nitrogen and a lessening of proteid. In fact, it is believed that this is a case of Salkowski's auto-digestion or autolysis, and will occur, not only in extracts, but also in the cells of the organ. Albumoses (but not peptone) and basic products are also formed. The autolysis differs in many important particulars from tryptic activity, particularly in selecting the globulin of the liver for destruction. The enzyme can be thrown down by ammonium sulphate, but more of this salt is needed than in the case of the liver aldehydase. The solutions obtained as the result of this autolytic activity are able to decompose solutions of hippuric acid with the formation of benzoic acid, and solutions of urea are decomposed also with the formation of ammonia, but whether this is due to the same or other enzymes is left an open question. The liver juice injected intravenously does not affect coagulation, but in a few experiments *in vitro* the coagulation of the blood was hindered, and in one case where coagulation took place 'fibrinolysis' occurred rapidly afterwards; boiling the juice did not affect this action. The autolytic decomposition of the liver is believed to occur *intra vitam* under conditions in which putrefaction is excluded, and increase in this normal function is stated to be the principal underlying pathological factor leading to the destruction of the liver substance and formation of leucine, tyrosine, ammonia, &c., in acute atrophy and phosphorus poisoning.

W. D. H.

Human Chyle. By THEODOR PANZER (*Zeit. physiol. Chem.*, 1900, 30, 113—116).—Owing to surgical interference, it became possible to obtain specimens of chyle from the thoracic duct of a woman.

It was alkaline, and became clear on shaking with ether. Microscopically, it showed fat particles and leucocytes. The proteids were albumin and traces of globulin, whilst albumoses, peptone, sugar, lecithin, urea, and uric acid were absent. Cholesterol, neutral fats, soaps, and a diastatic ferment were present. The inorganic salts were chiefly chlorides, sulphates, and phosphates of sodium and potassium. Four specimens were examined, and the main results are as follows:

Water	90.29 to 94.53 per cent.
Solids	5.47 „ 9.71 „
Organic substances	4.53 „ 8.91 „
Inorganic salts.....	0.8 „ 1.04 „
Coagulable proteid	2.16, one determination only
Substances soluble in ether...	6.59 „ „ „

W. D. H.

Properties and Formation of Lymph. By LEON ASHER and WILLIAM J. GIES (*Zeit. Biol.*, 1900, 40, 180—216).—This is another contribution to the much discussed question whether lymph is formed by purely mechanical processes. After intravenous injection of sugar, quinine does not influence the quantity or composition or amount of sugar in the lymph. This does not exclude a ‘physiological’ factor in lymph formation, even although quinine is a capillary poison. The action of ‘liver poisons’ (Heidenhain’s first class of lymphagogues) is inhibited by quinine. Liver activity is at least one ‘physiological’ factor, and quinine is known to lessen the action of this organ so far as its glycogenic and urea forming functions are concerned. The action of liver poisons cannot be simply explained as due to an increase of the permeability of the capillary walls in the liver. Arsenic is a typical ‘capillary poison,’ and leads to an increased flow of highly concentrated lymph. The injury to the vessel walls is much greater than that produced by crabs’ muscle and leech extracts, still the formation of lymph is greater if these weaker reagents are used. These facts are emphasised when it is considered that the formation of lymph goes on for a short time *post-mortem*. This is analogous to what occurs in *post-mortem* formation of saliva, and is a proof that the two depend upon similar physiological processes.

W. D. H.

Excretion in the Small Intestine. By CYRIL CORLETTE (*J. Physiol.*, 1900, 25, 344—355).—In a closed segment of ileum, a large mass accumulates, as originally shown by Hermann. The amount varies, and may depend on the amount of stimulation of the mucous membrane by bacterial products. Possibly some reabsorption occurs, and substances difficult of absorption like nuclein tend to accumulate. The mass contains iron, and calcium phosphate from the *débris* of shed cells; soaps are also present. More or less of the faecal pigment is derived from the shed bowel epithelium. None of the dogs experimented upon, five in number, exhibited any symptoms due to poisoning from bacterial products.

W. D. H.

Action of the Liquid of the External Prostate on the Liquid of the Vesiculæ Seminales. By L. CAMUS and EUGENE GLEY (*Compt. rend.*, 1900, 131, 351—353. Compare Abstr., 1899, ii, 779).—The secretion of Cowper’s glands or of the external prostate of the hedgehog produces an agglutinating action on the formed elements of the liquid secreted by the *vesiculæ seminales* and also the precipitation of a proteid substance in the same fluid.

W. D. H.

Properties of the Secretion of the Internal Prostate of the Hedgehog. By L. CAMUS and EUGÈNE GLEY (*Compt. rend.*, 1900, 131, 353—355).—The secretion of the internal prostate has the same properties as that of the external prostate (see preceding abstract). In the case of the internal prostate, however, this does not depend on the presence of the substance named vesiculin. W. D. H.

Peculiarities in the Urine of Vegetarians. By JOHN H. LONG (*J. Amer. Chem. Soc.*, 1900, 22, 592—595. Compare this vol., ii, 580).—Results are quoted of the analyses of the urine of seven men who, for a year or longer, had lived wholly on a vegetarian diet. The average daily excretion for a vegetarian appears to be 874 c.c. as against 1167 c.c. for non-vegetarians. If due allowance be made for the difference in concentration between a normal and vegetarian urine, the most striking feature is the small amount of creatinine in the latter, and this probably points to low metabolism, the subjects of experiment taking but little exercise. The reducing power due to carbohydrates and similar substances is somewhat higher than in the case of a normal urine. J. J. S.

Estimation of Amino-acid Nitrogen in Urine. By MEINHARD PFAUNDLER (*Zeit. physiol. Chem.*, 1900, 30, 75—89).—The total nitrogen of the urine was estimated in four fractions: (1) The nitrogen in the substances precipitable by phosphotungstic acid, which can be split off by phosphoric acid. This includes that from ammonia, carbamic acid, and a part of that from the uric acid, purine bases, urine-mucoid, and other proteids of normal urine. (2) The nitrogen in the same precipitate which cannot be split off by phosphoric acid; this includes the remainder of that from substances like uric acid, of which only a part of the nitrogen is firmly combined, also that from diamines, diamino-acids, and ptomaines. (3) The nitrogen which is easily split off in the urine *minus* the phosphotungstic precipitate; this includes that from urea, allantoin, oxaluric acid, and a part of the creatinine. (4) The firmly combined nitrogen in the substances not precipitable by phosphotungstic acid. This includes that from amino-acids and their derivatives, hippuric acid, taurine and cystine compounds, and in pathological urines, leucine, tyrosine, &c. In this last fraction, oxyproteic acid comprises from 41 to 46 per cent. of the whole. In urine containing albumin and albumose, the first fraction is increased by the amino-nitrogen of the proteids, and the second by Hausmann's mono- and di-amino-nitrogen. In all cases the ammonia can be estimated separately by Schlösing's method. The following table summarises the results obtained. The most marked result seen is the rise, in phosphorus poisoning, of the fourth fraction (due to amino-acids) and in the ammonia, at the expense, presumably, of the urea:

	Fraction 1	2	3	4	Ammonia.
Normal human urine	8·34	6·65	80·14	4·88	—
Dog. 1 normal urine	7·67	5·10	84·97	2·26	4·33
during phosphorus poisoning	7·73	5·24	81·89	5·13	5·77
Dog. 2 normal urine	7·00	2·24	86·43	4·33	4·03
during phosphorus poisoning	7·13	2·10	83·76	7·01	5·59

W. D. H.

Loosely Combined Sulphur in the Urine. By EUGEN PETRY (*Zeit. physiol. Chem.*, 1900, 30, 45—60).—The so-called 'neutral sulphur' of the urine is an ill-characterised quantity and is combined in various compounds. An important and easily determinable fraction of this, however, is that which can be readily split off as a metallic sulphide. In the dog on a mixed diet, and on a diet of flesh only, its amount varies slightly, namely, from 1 to 3 per cent. of the total sulphur. By feeding with casein, a proteid relatively poor in sulphur, the percentage varies from 3 to 3.15; with serum-albumin and serum-globulin from 1.1 to 2.2; with hetero-albumose (which contains a high percentage of easily dissociable sulphur), 5.5. Feeding with asparagus shoots has no influence. In phosphorus poisoning, the amount is slightly raised; in cases of liver cirrhosis and leucæmia, little departure from the normal is noticeable. Acetonitrile raises the amount, the increase being due to formation of thiocyanogen. Differences noted between different animals cannot be explained by variations in their diet. W. D. H.

Pseudomucin from Ovarian Cysts. By ZANGERLE (*Chem. Centr.*, 1900, i, 1035; from *Münch. med. Woch.*, 47, 414—415).—The pseudomucin from ovarian fluid yielded glucosamine after decomposition with hydrochloric acid. The reducing substance is therefore identical with that obtained by F. Müller from sputum and the sub-maxillary gland, and by Seemann from ovomucoid. In all these cases, the glucoproteid is a product of secreting cells. W. D. H.

Acetone Glycosuria. By WALTER RUSCHHAUPT (*Chem. Centr.*, 1900, i, 1036—1037; from *Arch. exp. Path. Pharm.*, 44, 127—141).—Acetone is present in normal urine in small quantities. In diabetes mellitus, the amount is increased. By acetone poisoning, produced by breathing acetone vapour, or by intravenous or subcutaneous injection of acetone, or by feeding on acetone, artificial glycosuria is produced. The sugar is derived from the carbohydrate constituents of the body, for in starving animals in which the glycogen has been reduced to a minimum, the glycosuria produced is very slight. W. D. H.

Antihæpatic Serum. By C. DELEZENNE (*Compt. rend.*, 1900, 131, 427—429).—Since the publication of Bordet's work (*Ann. Inst. Pasteur*, 1898—1900) on artificial hæmolytic serums, various observers have sought to prepare serums which act specifically on different groups of cells or organs. The present communication relates to a serum which acts injuriously on the liver cells. If an emulsion of dog's liver is injected intraperitoneally in rabbits and ducks, a serum is obtained from the blood of these animals which is strongly poisonous to the dog. If 2—4 c.c. of the serum are injected intraperitoneally or intravenously, death results, and the symptoms and *post-mortem* pathological appearances are almost exclusively of a hepatic nature. If death is rapid, the liver exhibits acute necrosis; if the animal lives a few days, the urea of the urine is lessened, and ammonia and amino-acids are increased; if carbohydrate food is given, there may be slight glycosuria; there is no

jaundice. After death, intense fatty degeneration of the liver cells is found. Small and gradually increasing doses of the serum create immunity; and the serum of an immunised animal has similar protective power.

W. D. H.

Syntheses in the Animal Organism. I. Piperidine Derivatives. By HERMANN HILDEBRANDT (*Chem. Centr.*, 1900, ii, 202—203; from *Arch. exp. Path. Pharm.*, 44, 278—316).—By the action of phenols and formaldehyde on piperidine, water is eliminated, and piperidides, which are usually crystalline compounds, are formed. "*Thymotinipiperidide*," $C_{16}H_{25}ON$, prepared from thymol, formaldehyde, and piperidine, melts at 149.5° . "*Carvacrylpiperidide*," similarly obtained from carvacrol, melts at 182° ; "*p-cresylpiperidide*" melts at 45° ; " *α -naphthylpiperidide*" and " *β -naphthylpiperidide*" melt at 135° and at 96° respectively.

The physiological action of thymotin-, carvacryl-, and *p*-cresylpiperidides on rabbits is, generally speaking, similar to that of piperidine. After administering thymotinipiperidide, the urine contains a glycuronic acid compound of "*methylthymotinipiperidide*"; it is a neutral crystalline substance, melts at 192° , and by boiling with hydrochloric acid yields a "*methylthymotinipiperidide*." Similar glycuronic acid compounds are obtained from other piperidides, and these substances are scarcely poisonous. By feeding with sucrose, dextrose, or maltose before administering the piperidide, its poisonous action is very much mitigated. Lævulose has a similar effect, but to a less extent, whilst lactose, galactose, dextrin, and mannitol are inactive in this respect; thus, it is only the sugars capable of forming glycogen in the organism which tend to form glycuronic acid compounds of these piperidides.

The physiological effects of the amide of tetramethylpyrroline-carboxylic acid, its reduction product, and the methylamide of 1-methyltetramethylpyrrolinecarboxylic acid were also investigated.

E. W. W.

May Phenolphthalein be safely added to Marc-Wines? By ZOLTAN VON VAMOSSY (*Chem. Zeit.*, 1900, 24, 679—680).—The author's experiments were undertaken at the request of Liebermann, who wished to ascertain whether small quantities of phenolphthalein may be added, without any ill effect, to margarine and also to marc-wines to facilitate recognition. Experiments conducted first on rabbits, and afterwards on himself and a colleague, showed that a dose of 1—1.5 grams has no other effect than that produced by saline draughts or castor oil, whilst the long continued use of daily doses of 0.1 gram produced no unpleasant symptoms whatever.

Considering that 1 gram of phenolphthalein is sufficient for 100 litres of wine, the small quantity thus introduced into the system can do no possible harm, particularly as the bulk of the phenolphthalein passes through the system undecomposed.

L. DE K.

Physiological Action of Poehl's Spermine. By WALTER E. DIXON (*J. Physiol.*, 1900, 25, 356—363).—Spermine injected intravenously produces a temporary fall of blood pressure, which is partly

of cardiac origin and partly due to dilatation of the splanchnic blood-vessels. This result is not influenced by nicotine or by section of the vagi. Atropine cuts out the fall of pressure without influencing the splanchnic dilatation. The spleen is constricted; the testis is dilated; the renal vessels follow the blood-pressure passively. Spermine and choline are about equally toxic, and the similarity in their action is extremely striking.

W. D. H.

Physiological Action of the Poisonous Secretion of the Gila Monster. By JOHN VAN DEUBURG and OTIS B. WIGHT (*Amer. J. Physiol.*, 1900, 4, 209—308).—A full account is given of experiments on dogs, cats, and frogs for the purpose of ascertaining the exact action on the various organs and functions of the body produced by the poison of the Gila Monster (*Heloderma suspectum*). The effects differ in no important respect from those of various snake venoms. No chemical examination of the poison itself is given.

W. D. H.

Iodine in Corals. By LAFAYETTE B. MENDEL (*Amer. J. Physiol.*, 1900, 4, 243—246).—Drechsel showed that the horny axial skeleton of the *Gorgonia cavolinii* contains iodine in organic combination. Several other workers have shown the same to be true for certain sponges and other marine organisms, and commented on the importance of iodine metabolism in certain animals. The present research shows the same is true for three other corals. The iodine apparently does not enter into the constitution of the true growing part of the animal. The following quantitative results are given; Drechsel's figures are added for comparison.

	Iodine.	Chlorine.
<i>G. cavolinii</i> (Drechsel)	7.79 per cent.	2.18 per cent.
<i>G. acerosa</i>	1.70 „	3.17 „
<i>G. flabellum</i>	1.15 „	1.24 „
<i>Plexora flexuosa</i>	0.28 „	0.86 „

W. D. H.

Colouring Matter of Echinus Esculentus. By ARTHUR B. GRIFFITHS (*Compt. rend.*, 1900, 131, 421—422).—The amorphous violet pigment of *Echinus esculentus* has the composition $C_{16}H_{12}ON_2$; when boiled with concentrated mineral acids, it yields leucine and formic acid.

W. A. D.

Chemistry of Vegetable Physiology and Agriculture.

Bacteriolysis of the Bacillus Anthracis. By G. MALFITANO (*Compt. rend.*, 1900, 131, 295—298).—Living protoplasm is believed to be capable of forming enzymes which ultimately destroy the protoplasm of the cells which produce them. Thus spontaneous destruction of bacteria (auto-bacteriolysis) is a possibility due to the production of a proteolytic enzyme by the bacteria. The experiments recorded

are stated to confirm this as a fact in the case of the *Bacillus anthracis*. Bacteriolysis occurs best in a neutral medium, and certain antiseptics are believed to owe their efficacy, not to their power of destroying protoplasm or counteracting enzymic action, but to the fact that, by altering the reaction of the medium, they allow spontaneous bacteriolysis to occur more readily.

W. D. H.

Gas Producing Power of *Bacillus Coli Communis* under Different Conditions of Environment. By MARY E. PENNINGTON and GEORGE C. KÜSEL (*J. Amer. Chem. Soc.*, 1900, 22, 556—567).—Cultures of this organism made on nutrient agar are most active, so far as gas production is concerned, when three days old, if kept at a temperature of 37°; older cultures produce less gas. The gas evolved under ordinary conditions consists of hydrogen 62—70, carbon dioxide 23—34, methane 1—4, and nitrogen 1—5 per cent. When grown in an apparatus from which oxygen is excluded, methane is not formed, and when grown in a medium free from meat extract, the amount of nitrogen evolved does not diminish.

There appears to be an intimate relationship between the reducing power which liberates hydrogen and that which produces nitrogen, but carbon dioxide is formed in largest quantity at the outset.

An apparatus consisting of two glass bulbs, one provided with a stopcock and attached to the other by rubber tubing, is recommended for experimental work of this kind.

J. J. S.

Physiology of Yeast. By EMILE DUCLAUX (*Chem. Centr.*, 1900, ii, 54—55; from *Allg. Hopf. Brauerz.*, 1900, 933).—A *resumé* and discussion of the physiological relationships of the yeast cell.

E. W. W.

Chemical Fermentation by Yeast in an Antiseptic Medium. By JOSEPH DE REY-PAILHADE (*Bull. Soc. Chim.*, 1900, [iii], 23, 666—668).—When brewer's yeast is quickly pressed and digested with a solution of maltose containing 1—1.2 per cent. of sodium fluoride, little action at first takes place, but after the third day a considerable evolution of carbon dioxide is noticed, and proteid substances are found to have entered into solution. In the first stage, the yeast is gradually destroyed by the antiseptic, whilst the later stage of more active change is due to the purely chemical action of ferments derived from the yeast. The evolution of gas is almost immediately arrested by the addition of sulphur, a fact which suggests that the ferments in question are closely related to philothion or hydrogenase (compare Abstr., 1899, i, 180).

N. L.

Germination. By LEON MAQUENNE (*Ann. Agron.*, 1900, 26, 321—332).—The results of the author's experiments indicate that the predominating, if not the only, rôle in the conservation and development of seeds must be attributed to the diastases, and that the causes which retard the alteration of the diastases tend to maintain the germinating power of the seeds. When preserved under conditions, of which absence of moisture is the most important, favourable to the diastases remaining inactive, seeds may be kept indefinitely.

N. H. J. M.

Influence of Pressure on Chlorophyllous Assimilation. By JEAN FRIEDEL (*Compt. rend.*, 1900, 131, 477—479).—Experiments made with various plants in an atmosphere containing 10 per cent. by volume of carbon dioxide and at pressures between 1.0 and 0.25 atmosphere, show that within these limits the nature of chlorophyllous assimilation is not altered, and the quotient O_2/CO_2 remains practically unity. The intensity of the assimilation, however, diminishes regularly with the pressure. C. H. B.

Ashes of some Medicinal Plants. By ARTHUR B. GRIFFITHS (*Compt. rend.*, 1900, 131, 422—423).—Full analyses are given of the ash of sarsaparilla, hydrastis, cardamom, oak, rhatany, and belladonna; manganese is present in all these plants. W. A. D.

Phosphorus Compound first formed in Chlorophyllous Plants. Physiological Rôle of Inositol. By POSTERNAK (*Ann. Agron.*, 1900, 26, 362—365; from *Rev. gén. bot.*, 12, 5 and 12).—The results of experiments with seeds of *Picea excelsa* showed that a relatively small amount of the phosphorus is contained in the proteids, the greater part being in the filtrates from the proteids. Several organic compounds rich in phosphorus were obtained from the solutions.

One of these compounds, "oxymethylphosphoric acid," CH_5O_5P , forms brilliant tablets and is very hygroscopic. Its composition indicates that it is an additive compound of phosphoric acid and formaldehyde, and its production is a direct proof that carbon dioxide is converted into formaldehyde before being utilised in the production of plastic matters. When its barium salt is distilled during 5 or 6 hours with 40 per cent. acid, there is no production of formaldehyde, but an almost pure solution of inositol is obtained.

It is suggested that inositol may be formed in plants when formaldehyde is produced in excess; whilst the glucose formed at the same time is capable of being directly assimilated, inositol would be a reserve substance, retaining the excess of formaldehyde in a convenient form so as to be at the disposal of the cells if required. N. H. J. M.

Citric Acid in Saturation-Sludge. By KARL ANDRÉLIK (*Zeit. Zuckerind. Bohm.*, 1900, 24, 645—648).—Besides oxalic acid, the sludge was found to contain citric acid (0.16 to 1.21 per cent. in the dry matter), and a small amount of what is probably tricarballic acid.

Michaelis detected citric acid in beet-root juice in 1851 (*J. pr. Chem.*, 54, 184; compare also C. Schrader, *Annalen*, 1862, 121, 370).

N. H. J. M.

Presence of Vanillin in Vanilla. By JOHANNES BEHRENS (*Bied. Centr.*, 1900, 29, 547—549; from *D. Tropenpflanzer*, 1899, 299).—The fact that ripe vanilla has no odour may be due to the odour of vanillin being retained by the living protoplasm, or, as is more probable, the production of vanillin may only occur after the death of the fruit-cells. It was found that fresh leaves, or an extract of the leaves, acquire a distinct odour of vanillin when heated with dilute sulphuric or hydrochloric acid for 2 hours at 100°. The leaves contain, therefore, a soluble substance having the properties of a vanilla-glucoside. In the

natural treatment of the fruit, the breaking up into vanillin and sugar would be brought about by an enzyme. N. H. J. M.

Nitrogenous Substances in Malt. By PAUL PETIT and G. LABOURASSE (*Compt. rend.*, 1900, 131, 394—396).—The authors denote the nitrogen precipitated with phosphotungstic acid and with zinc sulphate by *A* and *B* respectively, and that present in the ammonia evolved on boiling with dilute hydrochloric acid for 2 hours, by *C*; the nitrogen *A* is probably that of peptones, *B* that of albumoses, and *C* that of aminic substances. After adding hops and boiling for 2½ hours the nitrogen *A* and *C* of the malt, when water containing a small quantity of calcium sulphate is used, is partly changed into the form *B*; when sodium chloride is present in the water instead, the tendency is for *A* to change into *C*, *B* remaining constant; whilst with calcium hydrogen carbonate the change is less marked, *A* being formed at the expense of *B* and *C*. Saccharification is thus largely influenced by the nature of the mineral matter in the water employed. During fermentation, relatively small amounts of *C* are assimilated by the yeast, except in the presence of sodium chloride, when the proportion of *C* removed is large and that of *A* practically nil; the proportions of *A* and *B* absorbed, especially the latter, are large in all cases. W. A. D.

Milky Juice of *Hura Crepitans*. By J. J. SURIE (*Chem. Centr.*, 1900, i, 1210—1211; from *Ned. Tijds. Pharm.*, 12, 107—116).—The milky juice of *Hura crepitans* is an acid liquid of sp. gr. 1·05—1·06; it has a lingering, burning taste, and causes violent inflammation and swelling of the skin. The poisonous constituent, *hurin*, may be extracted by ether; it is volatile in steam, has a faint acid reaction, melts at 23°, and even in the form of vapour causes inflammation and eczema. E. W. W.

Analyses of Marine Algæ. By L. CUNIASSE (*Chem. Centr.*, 1900, ii, 286—287; from *Ann. Chim. anal. Appl.*, 5, 213—215).—The aqueous extract of 100—200 grams of ash is evaporated to dryness, and the residue distilled with manganese dioxide and sulphuric acid, the vapours being absorbed in aqueous caustic alkali. Iodine is precipitated with palladium nitrate, bromine and chlorine with silver nitrate.

The ash of the richer varieties of sea algæ contain, Br, 0·192—0·423; I, 0·602—1·408; Na₂O, 8·13—26·50, and K₂O, 8·70—23·03 per cent.; that of the poorer kinds, Br, 0·039—0·161; I, 0·070—0·157; Na₂O, 8·50—16·25, and K₂O, 10·80—18·20 per cent. L. DE K.

Experiments at Grignon. By PIERRE P. DEHÉRAIN (*Ann. Agron.*, 1900, 26, 369—383. Compare this vol., ii, 303).—Field experiments with varieties of potatoes, and smaller experiments on the effect on potatoes of green manuring with vetches are described.

Mangolds. The object of these experiments, which were made in large boxes of 4 cubic m. capacity was to ascertain the effect of irrigation on the growth of mangolds. No. 1 was manured with vetches and was not watered; No. 2 had no green manure, but was watered; and No. 3 was manured with vetches and was watered. The yield of dry matter, sugar, and nitrogen was considerably greater in 2 than in 1;

in 3 rather more dry matter and nitrogen and rather less sugar were obtained than in 2. The results apply only to a good soil resting on an impermeable and inclined subsoil.

Sainfoin and Lucerne. When sainfoin and lucerne are sown together at Grignon, the sainfoin predominates during the first two years, and then disappears. In 1897, several plots were sown with the mixed seed; no manure was applied. In 1899, gramineous herbage appeared on the plots, and a variety of manures were applied. The manures had very little effect on the yield, but whilst the herbage from the sodium nitrate plot contained 18·5 per cent. of *Gramineæ*, the hay manured with potash and superphosphate contained only 15·5 per cent. In 1900, there was so much inferior grass that the experiment was discontinued.

It is thought possible that the failure may be due to the vigorous growth of sainfoin having weakened the lucerne, and rendered it incapable of resisting the encroachment of the grasses, but it is also possible that leguminous crops have been grown too long.

N. H. J. M.

Value of Molasses as Food. By PAUL HOPPE (*Zeit. Ver. Deut. Zuckerind.*, 1900, 535, 713—762).—It is of importance to ascertain the nature of the molasses employed as food; acid molasses should be rejected.

In experiments with cows, it was found that large amounts of molasses, 5 kilos. per day, did not interfere with digestion, and had no purgative action. It is thought that the purging sometimes observed by others is not only, or mainly, due to the salts present in the molasses, but to the saccharates.

In the cases of cows recently calved, molasses acted only on the production of milk; during gestation, however, molasses was favourable both as regards milk production and in increasing the live weight.

Whilst molasses increased the yield of milk, the percentage of fat was distinctly diminished when large amounts of molasses were employed; the percentage of nitrogen remained unaltered, and the acidity was increased. Molasses had no effect on the butter.

Dried molasses is preferable to liquid molasses, and forms a good substitute for mangolds. The dried substance is not only very favourable to milk production, but also increases the live weight.

N. H. J. M.

Blood Molasses. By FRIEDRICH STROHMER (*Chem. Centr.*, 1900, ii, 135—136; from *Oesterr.-ung. Zeit. Zucker-Ind. Landw.*, 29, 161—172).—The food is prepared by drying and sterilising a mixture of blood (4 parts) and molasses (1 part) with bran or brewers' grains. According to Maercker, 95·9 per cent. of the proteids is digestible. Satisfactory results of feeding experiments with blood molasses were obtained by Ramm and Mintrop (*Milch-Zeit.*, 27, 519, and this vol., ii, 39) and by Lilienthal (this vol., ii, 502).

As regards the amount of blood available, it is stated that the Vienna slaughter-houses furnished 6,000,000 kilos. in one year.

N. H. J. M.

Feeding Pigs with Blood Molasses. By LILIENTHAL (*Bied. Centr.*, 1900, 29, 526—527; from *Deut. Landw. Presse*, 1899, 74; compare this vol., ii, 502).—The results of experiments with pigs showed that there was at first an increase in weight due to feeding with blood molasses, but that finally the weights were considerably less than with maize and barley (in addition to skim-milk and roots). The molasses did not interfere with the health of the pigs, but injured the quality of the meat; the fat was watery, and some of it of a spongy texture.

It is thought that it may be possible to prepare a food suitable for pigs from blood molasses. N. H. J. M.

Peat-meal Molasses. By RUDOLF WOY (*Chem. Centr.*, 1900, ii, 284; from *Zeit. öffent. Chem.*, 6, 201—204).—Whilst peat-meal shows a slightly acid reaction, the addition of alkaline molasses renders it strongly acid, without, however, affecting essentially the amount of alkali required to neutralise it. During prolonged storage, the sugar becomes inverted by the acid of the peat unless this is rendered neutral.

The amount of sugar present is determined as follows. The food (16·5 grams) is extracted on a funnel with boiling water, the solution treated with lead acetate when cold, and diluted to 300 c.c. Two hundred c.c. of the filtered solution are freed from lead by means of sodium phosphate solution (20 c.c.), and 50 c.c. inverted by heating for 20 minutes in water heated to 67—70° with 5 c.c. of 20 per cent. hydrochloric acid. The inverted solution is then diluted to 250 c.c., of which 50 c.c. is employed for determining the sugar by Kjeldahl's method. The invert sugar (in eg. from Kjeldahl's tables) doubled and multiplied by 0·95 gives the percentage of cane sugar in the food. Assuming the molasses to contain 48 per cent. of cane sugar, the relation of peat to molasses can be ascertained sufficiently exactly.

In the above method, the raffinose will be included in the results as cane sugar. This is, however, of no practical importance, as raffinose is presumably as readily digested as cane sugar.

A polarimetric method for determining the sugar is described, but as a rule the gravimetric method is preferable. N. H. J. M.

Feeding Experiments with Crushed Palm Kernels. By PAUL VIETH (*Chem. Centr.*, 1900, ii, 136—137; from *Milch. Zeit.*, 1900, 294—295).—Six cows were fed with straw, hay, chaff, dried brewers' grains (1000 grams), rape cake (250 grams), peat molasses (500 grams), maize gluten meal (250 grams), and stored beetroot sections (20 kilograms) per head per day. In addition, the cows received either crushed palm kernels (2 kilos.) or cotton-seed meal (0·5) and wheat bean (1·5 kilograms). Although the palm kernels gave only slightly better results as regards the yield of milk, fat, and total dry matter, its employment is strongly recommended owing to its less cost. N. H. J. M.

Composition of Various Kinds of Peat. By BRUNO TACKE and BERNHARD TOLLENS (*Bied. Centr.*, 1900, 29, 508—509; from *J. Landw.*, 1898, 46, 341. Compare H. von Feilitzen, *ibid.*, 46, 9).—The

samples of peat were of German, Hungarian, and Russian origin, and contained from 54.5 to 57 per cent. of carbon, with the exception of one which contained 64.32 per cent. (in the substance free from ash). The amounts of ash, organic matter, carbon, hydrogen, nitrogen, and oxygen in all the samples are given. The percentage of nitrogen in organic matter varied from 3.96 to 6.86 per cent. N. H. J. M.

Composition of Drainage from Unmanured and Manured Peat Soil, with special reference to Nitrogen Compounds. By BRUNO TACKE, HEINRICH IMMENDORFF, and H. MINNSEN (*Bied. Centr.*, 1900, 29, 505—508; from *Landw. Jahrb.*, 1898, *Erg.-bd.*, iv, 349).—The peaty soil, contained in pots, was manured with lime, and with lime, kainite, and basic slag both with and without addition of sodium nitrate; there were also check experiments without manure.

It was found that a portion of the organic nitrogenous matter of peat is readily decomposed, with production of ammonia and nitrates; most of the nitrogenous matter is, however, very stable, and its decomposition is not promoted by the normal amount of lime as this does not completely neutralise the acidity of the soil. Large amounts of lime promote nitrification considerably. Manuring with lime, kainite, and phosphate does not appreciably increase the amount of ammonia in the drainage, but there was a distinct increase in ammonia when sodium nitrate was applied in addition to the mineral manures.

Both the pre-existing phosphoric acid and that applied as manure are retained by peat with considerable tenacity, but when phosphates are applied continuously the retentive power of the soil seems to diminish.

With regard to potash, magnesia, and lime, small portions of these constituents present in natural peat-land are relatively readily soluble in water; the greater portion is, however, sparingly soluble. Much of the potash applied as manure is liable to loss in drainage, whilst the rest is retained by the soil.

Manuring with potash increases the solubility of the lime very considerably. N. H. J. M.

Changes in the Weights of Artificial Manures when Exposed to Air. By L. VON WISSELL (*Chem. Centr.*, 1900, ii, 282—283; from *J. Landw.*, 48, 116—121).—Fifty grams of each manure were exposed to the air in flat dishes covered with perforated paper. Basic slag changed very little, notwithstanding the free lime which it contains, the maximum gain being 0.6 per cent. Superphosphate showed, according to the temperature and condition of the atmosphere, the maximum loss and gain of -3.7 and +9.3 per cent. Kainite and sodium nitrate lost in weight in warm, dry weather, but in damp air the weight increased by as much as 31 and 11.1 per cent. respectively. One sample of ammonium sulphate gained 5 per cent. in weight, whilst a second sample was only slightly hygroscopic.

N. H. J. M.

Manurial Experiments with Green and Dead Plants and Parts of Plants. By EWALD WOLLNY (*Bied. Centr.*, 1900, 29, 509—523; from *Vierteljahresschr. Bay. Landw.-rat.*, 1897, Heft. 3 and 4).—In the case of soils poor in humus and nitrogen, green manuring

with leguminous plants, supplemented with potash, phosphates, and lime, is far more effective than when non-leguminous plants are employed. On highly nitrogenous soils, the effect of manuring with leguminous plants is the same as with non-leguminous. The ploughing in of plants on the land where they were grown is less effective than when the crop is removed to fallow land. Manuring with straw had a relatively slight effect. Pea and bean straw gave, on the whole, better results than rye and rape straw.

The application of peat was, as a rule, very beneficial. Sandy soil, when manured with peat, retained more water, whilst loam was rendered more porous.

Experiments are described in which winter rye was grown on plots from which the residues of the previous crops had been removed, and on plots containing the residues. The results showed that the removal of the crop residues diminished the yield. The most valuable crop residues are those of clovers, then those of root-crops and potatoes, and last, the stubble and roots of cereals.

N. H. J. M.

Influence of Bacteria on the Decomposition of Bones. By JULIUS STOKLASA, F. DUCHÁČEK, and J. PITRA (*Zeit. Zuckerind. Bohm.*, 1900, 24, 627—645).—Sifted bone meal (in quantities of 10 grams) with water (900 c.c.), potassium sulphate (0.1 gram), magnesium chloride (0.05 gram), and ferric sulphate (0.01 gram) was sterilised, and then inoculated with various bacteria. The following percentage amounts of nitrogen in different forms, and of dissolved phosphoric acid (per cent. of total) were found at the end of the experiment, which lasted 33 days.

	Amide nitrogen.	Diamine nitrogen.	Monamine nitrogen.	P ₂ O ₅ , in solution.
Not inoculated.....	4.33	28.72	61.51	3.83
<i>Bacillus megatherium</i> (alinit) ...	61.04	20.48	14.05	21.56
„ <i>fluorescens liquefaciens</i>	22.60	56.80	15.40	9.19
„ <i>proteus vulgaris</i>	43.57	29.62	28.54	14.79
„ <i>butyricus</i> , Hueppe.....	45.85	14.42	35.57	15.55
„ <i>mycoides</i>	62.15	8.62	25.05	23.03
„ <i>mesentericus vulgatus</i> ...	63.05	40.96	—	20.60

Vegetation experiments are described in which oats grown in large pots were manured with bone meal and inoculated with the different bacteria. Dextrose was applied to the inoculated pots. The results accord with those described above. In the case of *B. megatherium*, one pot was without dextrose. Whilst in this case the yield of oats was far greater than without inoculation, the addition of dextrose gave rise to a further increase. Xylose, in the place of dextrose, produced a still greater increase in the pot inoculated with *B. megatherium*.

The soil employed for these experiments was not sterilised before being inoculated.

N. H. J. M.

Infected Phosphates. By HUGO BORNTAGER (*Chem. Centr.*, 1900, ii, 283; from *Oesterr. Chem. Zeit.*, 3, 235).—A sample of ammonium phosphate acquired an intense odour of putrid urine, whilst potassium phosphate became covered with red and blue algæ. As superphosphates

may become similarly infected, it is proposed to add to them free humic acid, from peat, or else Cassel brown or lignite. In this manner, both infection and the production of insoluble phosphoric acid would be prevented.

N. H. J. M.

Analytical Chemistry.

Employment of Floats in Burettes. By KREITLING (*Zeit. angew. Chem.*, 1900, 829—836).—A lengthy investigation as to the use of floats in burettes. The results are given in tabular form. The conclusion reached is that their use should be avoided.

L. DE K.

[Electrometric Estimation of Iodine]. By F. CROTOGINO (*Zeit. anorg. Chem.*, 1900, 24, 225—262).—See this vol., ii, 642.

Detection of Iodic Acid in the Presence of Chloric Acid, Bromic Acid, Perchloric Acid, and Periodic Acid by means of Morphine Sulphate. By C. REICHARD (*Chem. Zeit.*, 1900, 24, 644—646).—Potassium iodate may be recognised in the presence of potassium bromate and perchlorate by adding some morphine sulphate and a little sulphuric acid, when a brown precipitate, or according to the amount of dilution, a brown, yellowish-brown, or yellow coloration is produced; the reaction may be obtained at still greater dilutions by adding some ammonia at the beginning of the reaction, but the coloration then takes some time to develop. If potassium periodate is present, it may be isolated by treating the mixture with a little cold water, in which it is practically insoluble. Potassium periodate also gives a similar but less marked reaction with morphine sulphate.

The reaction is interfered with by the presence of arsenious and sulphurous acids.

L. DE K.

Apparatus for the Determination of Ammonia in Water by the Wanklyn Method, and Total Nitrogen by the Kjeldahl Method. By ROBERT SPURR WESTON (*J. Amer. Chem. Soc.*, 1900, 22, 468—473).—A detailed description of a modified form of distillation apparatus suitable for cases where a large number of estimations are carried on at the same time. The point aimed at is that the distilling flasks, burners, and receivers are all at the front of the apparatus and so readily accessible. For details, the drawings in the original must be consulted.

E. G.

Comparative Estimations of Nitrogen in Saltpetre. By L. VON WISSEL (*Chem. Centr.*, 1900, ii, 212; from *J. Landw.*, 48, 105—115).—The author has investigated Möckern's process (reduction of nitrates with zinc and iron powder in an alkaline solution), Ulsch's process (reduction with reduced iron and sulphuric acid), Forster's process (reduction with sulphosalicylic acid and sodium thiosulphate), and Devarda's process (reduction with aluminium-zinc-copper).

The last is, in the author's opinion, the most accurate and rapid ; the following proportions are recommended : 50 c.c. of the solution of nitrate (0.5 gram solid), 120—145 c.c. of water, 7.5—9 c.c. of alcohol, 75—90 c.c. of aqueous potassium hydroxide (sp. gr. 1.3) or 75 c.c. of aqueous sodium hydroxide (sp. gr. 1.34) and 3.5—4.5 grams of aluminium-copper-zinc alloy.

L. DE K.

Gasometric Method of Estimating Nitrites in Presence of Nitrates or other Soluble Salts. By J. GAILHAT (*J. Pharm.*, 1900, [vi], 12, 9—12).—All air is initially expelled by boiling from the flask of a Schloësing's apparatus for estimating nitrates, two-thirds filled with concentrated aqueous ammonium chloride ; 10 c.c. of the solution to be titrated, containing from 5—10 grams of nitrite per litre, are then gradually added, and the nitrogen evolved quantitatively according to the equation $\text{NH}_4\text{Cl} + \text{M}'\text{NO}_2 = \text{N}_2 + 2\text{H}_2\text{O} + \text{M}'\text{Cl}$, measured in a graduated tube completely immersed in cold water. Experiments are cited showing the degree of accuracy of the method.

W. A. D.

Iodometric Estimation of Arsenic Acid. By FRANK A. GOOCH and JULIA C. MORRIS (*Amer. J. Sci.*, 1900, 10, 151—157).—Williamson's process, namely, liberating iodine by adding potassium iodide and a sufficiency of hydrochloric acid to a weak solution of the arsenate and titrating with sodium thiosulphate, suffers from some sources of error. Owing to the large amount of acid, there is a danger of iodine being liberated from the potassium iodide by the action of the air and the acid may also cause partial decomposition of the thiosulphate ; these two errors somewhat compensate one another. Then again, starch cannot be used as indicator in the presence of strong acid. After being bleached, the liquid may be neutralised with potassium carbonate (not hydroxide), excess of potassium hydrogen carbonate added, and the arsenious acid titrated as usual with iodine. When using Williamson's process, it must be remembered that should there be a deficiency of acid the reaction becomes reversible.

Although the authors have proved by a series of experiments that the process may be improved by deducting 0.0030 gram of arsenic acid when using the direct titration with thiosulphate, and 0.0015 gram when titrating the alkaline liquid with iodine, they still prefer the method proposed by Gooch and Browning (*Abstr.*, 1891, 244). In this process, the arsenic acid is reduced by boiling with dilute sulphuric acid and potassium iodide, the last trace of free iodine is bleached with sulphurous acid, and the cold and neutralised liquid is then titrated as usual with standard iodine.

L. DE K.

Process for the Estimation of Carbon Dioxide in Carbonates. By R. E. DIVINE (*J. Amer. Chem. Soc.*, 1900, 22, 473—476).—An account is given of a simple and accurate method in which the carbon dioxide is liberated by means of sulphuric or tartaric acid and absorbed by solution of barium hydroxide, the excess of which is determined by titration with standard hydrochloric acid. The apparatus is fully described with the aid of a diagram.

E. G.

Detection of Metals by the Absorption Spectra of their Compounds with Alkanna. By JULIUS FORMANEK (*Zeit. anal. Chem.*, 1900, 39, 409—434).—The neutral chlorides and nitrates of the following metals give more or less characteristic absorption spectra with an alcoholic extract of alkanna root, to which a trace of ammonia is added: iron, caesium, potassium, rubidium, sodium, cobalt, barium, strontium, lithium, nickel, manganese, calcium, magnesium, zinc, copper, and aluminium; and without addition of ammonia: iron, uranium, nickel, copper, aluminium, and beryllium. The remaining metals produce no alteration of the alkanna spectrum. A single flint glass prism of 60° should be used in order that the spectrum may not be too much extended.

The extract of alkanna root with 95 per cent. alcohol should be of such concentration that its own absorption bands are well defined. To 5 c.c. of this extract, in a test-tube of 10—12 mm. diameter, a few drops of the metallic solution are added, and after observing the spectrum, a trace of dilute ammonia, but not enough to produce a precipitate, is added. In the case of the alkali metals, the bands disappear after a time; those of the alkaline earths gradually shift towards the red; with aluminium, the development of the bands requires time. When two metals are present, it sometimes happens that the bands peculiar to each are not simultaneously present, but new bands of intermediate position are produced. In other cases, the presence of one metal will completely suppress the spectrum due to another.

M. J. S.

Estimation of Total and Free Alkali and Alkali Carbonate in Soaps. By ROBERT HENRIQUES and OTTO MAYER (*Zeit. angew. Chem.*, 1900, 785—788).—Five to ten grams of soap are dissolved in 100 c.c. of water contained in an Erlenmeyer flask. When cold, the flask is closed with a treble-perforated cork through the centre of which passes a separating funnel; through one of the other holes passes a bent tube reaching to the bottom of the flask and connected at the other end with a wash bottle containing aqueous sodium hydroxide, and through the third hole passes a bent tube connected with a drying bottle containing sulphuric acid, a tube containing calcium chloride and a weighed potash bulb apparatus; the last is then connected with an aspirator.

A known volume of $N/2$ hydrochloric acid is introduced into the flask, the funnel is slightly rinsed, and the aspirator is set in action. Gentle heat is now applied so that the soap is fully decomposed in about half or three-quarters of an hour, and the air current is then kept up for about another hour when the bulb-apparatus is weighed. From the carbon dioxide thus found, the amount of alkali carbonate is calculated.

The liquid in the flask is heated, and the fatty acids are filtered off and washed with boiling water until free from acidity; the filtrate is then titrated with $N/2$ alkali. The fatty acids are dissolved in boiling alcohol, the filter is thoroughly washed, and the filtrate also titrated with $N/2$, preferably alcoholic, alkali; as a check, the solution may be evaporated to dryness and the pure soap weighed. From these results, the amounts of total and free alkali are readily calculated. The process

becomes a little more complicated when the fats employed in the manufacture of the soap contain soluble fatty acids. In this case, the total fatty acids of the sample must be estimated by decomposing the soap with dilute hydrochloric acid in the presence of ether. After carefully washing the ethereal solution with a little cold water, it is titrated with $N/2$ alcoholic alkali. L. DE K.

Method for the Rapid Gravimetric Estimation of Calcium. By WILLIAM H. HESS (*J. Amer. Chem. Soc.*, 1900, 22, 477—478).—The following method for the estimation of calcium, in which it is weighed as sulphate, is both rapid and accurate. Calcium oxalate is precipitated in the usual way and ignited; the residue of lime is treated with about its own bulk of dry ammonium nitrate and about twice as much fused ammonium sulphate, and gradually heated until fumes of ammonium salts cease to be driven off. By this means, the whole of the lime is converted into calcium sulphate. E. G.

Titration of Zinc with Potassium Ferrocyanide. By EDMUND H. MILLER and E. J. HALL (*Chem. Centr.*, 1900, ii, 146—147; from *School of Mines Quarterly*, 21, 267—272).—When titrating zinc in hydrochloric acid solution with potassium ferrocyanide, using uranium acetate as indicator, the liquid should not contain calcium chloride or aluminium sulphate; magnesium sulphate, although interfering with the titration in an ammoniacal solution, does not affect it in an acid liquid. Traces of lead do not interfere, provided there is a sufficiency of free acid, but it has been found that a large excess of acid is in itself a source of error. Ammonium chloride should also be absent, as it dissolves some zinc ferrocyanide. Traces of bismuth do not interfere, but antimonious chloride does so appreciably. L. DE K.

Electrolytic Estimation of Cadmium. By DMITRI BALACHOWSKI (*Compt. rend.*, 1900, 131, 384—387).—All previously described methods of precipitating cadmium electrolytically are too slow and give a too loosely adherent deposit to be of use in analysis; the necessary details are now given for the quantitative deposition of the metal. Aqueous solutions of the sulphate are used containing either acetic acid, urea, formaldehyde, or acetaldehyde. W. A. D.

Action of Sodium Thiosulphate on Lead Salts. By FRANZ FAKTOR (*Chem. Centr.*, 1900, ii, 239—240; from *Pharm. Post*, 33, 355).—A boiling concentrated solution of sodium thiosulphate added to a boiling solution of lead nitrate produces a white precipitate which does not become black on prolonged boiling. When the lead has been converted into chloride by means of sodium chloride, the precipitate becomes partly converted into sulphide on prolonged heating. If, however, ammonium chloride is used instead of the sodium salt, sodium thiosulphate produces at once a precipitate of heavy, black lead sulphide. L. DE K.

Analyses of Lead and Tin Ores, also of the most important Lead and Tin Preparations and their Commercial Products. By H. MENNICKE (*Chem. Centr.*, 1900, ii, 287—288; from *Zeit. offentl. Chem.*, 6, 190-194, 204—213).—The author treats the lead or tin

compound with hot, dilute hydrochloric acid and metallic zinc, best in the presence of platinum. The metallic lead is washed with dilute hydrochloric acid, then with alcohol, and after being dried in a current of coal gas, is weighed. The metallic tin may be weighed as such, or it may be redissolved in strong hydrochloric acid in a current of carbon dioxide, and titrated with the usual precautions with potassium permanganate. About 2 milligrams of metallic tin escape the action of the zinc and should be allowed for.

L. DE K.

Analysis of Phosphor-copper. By HUGO BORNTAGER (*Zeit. anal. Chem.*, 1900, 39, 360).—Half a gram of the substance is dissolved in 10 c.c. of nitric acid of sp. gr. 1.4, the solution is made strongly alkaline with ammonia, and filtered from carbon, ferric oxide, and silica. The copper in the filtrate is thrown down by ammonium sulphide and ignited by Rose's method. In the filtrate from the copper sulphide, the phosphoric acid is precipitated by magnesia mixture after concentrating.

M. J. S.

Titration of Mercury by Sodium Thiosulphate. By JOHN T. NORTON, jun. (*Amer. J. Sci.*, 1900, 10, 48—54).—Scherer has proposed a process for the volumetric estimation of mercurous nitrate, mercuric nitrate, or mercuric chloride by direct titration with sodium thiosulphate without the aid of an indicator. The author states that the process breaks down with mercurous or mercuric nitrates, but, with a slight modification, accurate results may be obtained with mercuric chloride when the amount of this does not exceed 0.1 gram.

The solution is placed in a litre flask, diluted to 100 c.c., and heated to 60°. *N/20* solution of sodium thiosulphate is now added from a burette until the white precipitate turns slightly brown. The liquid is diluted with cold water, a little asbestos fibre added, and the whole well shaken and poured on to an asbestos filter placed on a perforated platinum cone which is fixed in a glass funnel by means of a rubber connection; the funnel passes through the stopper of a large, side-necked Erlenmeyer flask connected with an exhaust pump. After carefully washing the precipitate, the filtrate is mixed with 3 grams of potassium iodide, and the excess of thiosulphate estimated as usual by means of *N/20* iodine. One c.c. of *N/20* sodium thiosulphate represents 0.015 gram of metallic mercury.

L. DE K.

Simple and Accurate Method for the Estimation of Mercury in Urine. By P. FARUP (*Chem. Centr.*, 1900, ii, 213—214; from *Arch. exp. Path. Pharm.*, 44, 272—277).—About 1 litre of urine is mixed with 3—4 c.c. of hydrochloric acid, heated in a water-bath to 70—80°, and shaken for 2 minutes with 6 grams of zinc dust. When cold, this is collected on a filter of silky asbestos. This is then put back into the flask and treated with hydrochloric acid and potassium chlorate. In this solution, the mercury is precipitated by stannous chloride, collected on gold-asbestos, and weighed.

L. DE K.

Estimation of Mercury in Urine. By J. WERDER (*Zeit. anal. Chem.*, 1900, 39, 358—359).—The method published by Schumacher and Jung (this vol., ii, 247) is incomplete, inasmuch as no confirmation is furnished that the loss of weight suffered by the gold asbestos

when ignited is really due to the presence of mercury. This proof can be supplied by connecting the asbestos filter tube containing the amalgamated gold with a bulb tube through which a current of air is aspirated. The connection is made by a plug of asbestos, and, by suitably heating, the mercury expelled is collected in the bulb, where it can be identified by aspirating over it the vapour of iodine which converts it into the red iodide.

M. J. S.

Examination of Aluminium and Zinc by Solution in Hydrochloric Acid. By F. BALDY (*Chem. Centr.*, 1900, ii, 238—239; from *Ann. Chim. anal. appl.*, 5, 201—205).—The metal (0.5—1 gram) is placed in a flask with 40 c.c. of water, and then dissolved by adding 10 c.c. of a mixture of 4 volumes of hydrochloric acid of sp. gr. 1.02 with 1 volume of nitric acid of sp. gr. 1.334. The gases evolved, after passing through a condenser, are freed from hydrochloric acid by means of ferrous sulphate, the carbon dioxide then absorbed by means of calcium succinate and estimated by titration. The metals are precipitated from a portion of the acid solution by sodium hydroxide and in the filtrate the sulphuric acid is estimated, whilst another portion of the solution is used for the estimation of phosphorus and arsenic.

The aluminium is separated from the iron by potassium hydroxide and determined as phosphate. In the case of zinc, the iron and lead are precipitated by ammonia, and the zinc and cadmium separated by potassium hydroxide.

E. W. W.

Volumetric Estimation of Manganese in Pig-iron, Cast-iron, and Steel. By ANDRÉ MIGNOT (*Chem. Centr.*, 1900, ii, 65—66; from *Ann. Chim. anal. appl.*, 5, 172—177).—The sample is dissolved in 25 times its weight of nitric acid of sp. gr. 1.2, heated to boiling, diluted with water and mixed with three times its weight of bismuth tetroxide. The pink solution is then filtered through asbestos, and the permanganic acid titrated with hydrogen peroxide. The process is not applicable in the presence of chromium if this exceeds 1 per cent.

Bismuth tetroxide is prepared by fusing in an iron dish equal parts of bismuth subnitrate and potassium chlorate with 2 parts of sodium hydroxide; the mass is then extracted with water to remove the alkali and dried.

L. DE K.

Precipitation of the Sulphides of Nickel and Cobalt in an Alkaline Tartrate Solution. By OLIN F. TOWER (*J. Amer. Chem. Soc.*, 1900, 22, 501—521).—In employing the method suggested by Villiers (*Abstr.*, 1895, ii, 228, 247) for the qualitative separation of nickel and cobalt, it is found that the oxidation of the solution to which the hydrogen sulphide has been added results in the separation of so much sulphur that, if nickel is present and cobalt absent, the black solution will colour the sulphur, making it very difficult to distinguish it from precipitated cobalt sulphide; it is also observed that the sodium chloride present in the solution may cause some nickel sulphide to be precipitated which may be easily mistaken for cobalt sulphide. Experiments are described which show that nickel sulphide in solution in an alkaline tartrate is in the colloidal state.

E. G.

Action of Sodium Thiosulphate on Certain Metallic Salts, and its Employment in Quantitative Analysis. By FRANZ FAKTOR (*Zeit. anal. Chem.*, 1900, 39, 345—354).—Under certain conditions, sodium thiosulphate can be used for the estimation of the chromium in chromates and chromic salts. From a solution of potassium chromate or dichromate, to which ammonium chloride or magnesium chloride is added, the whole of the chromium is precipitated as chromium chromate (mixed with sulphur) by boiling with an excess of sodium thiosulphate. The precipitate is converted into pure chromic oxide by ignition. From chromic chloride, the whole of the chromium is not precipitated unless a small quantity of a chromate is also present.

Lead chloride or lead nitrate mixed with ammonium chloride (but not if sodium chloride is substituted) readily yields the whole of its lead as sulphide when heated with an excess of thiosulphate. Silver nitrate also yields all its silver as sulphide when warmed with sodium thiosulphate. Nickel and cobalt yield sulphides, but the precipitation is in neither case complete. M. J. S.

Volumetric Estimation of Chromic Acid by Arsenious Acid in an Alkaline Solution. By C. REICHARD (*Chem. Zeit.*, 1900, 24, 563—564).—A known weight of pure arsenious oxide is dissolved in 10 per cent. aqueous sodium hydroxide and the exact strength of the solution is ascertained by titrating with either standard iodine or standard permanganate.

The chromate to be analysed is boiled for some time with a known volume of the alkaline arsenious oxide solution; this causes the separation of some of the chromium hydroxide, which is removed by filtration through a sieve-like porcelain funnel. The filtrate is then nearly neutralised with dilute hydrochloric acid, excess of sodium hydrogen carbonate is added, and the excess of arsenious acid estimated as usual by means of iodine.

To avoid the filtration, the liquid may be mixed with excess of dilute sulphuric acid, any undissolved chromium hydroxide washed by decantation, and the excess of arsenious acid titrated with standard potassium permanganate. The test-analyses are satisfactory.

L. DE K.

Estimation of Molybdenum in Iron. By E. DOHLER (*Chem. Zeit.*, 1900, 24, 537).—The sample is dissolved in nitric acid and the solution evaporated to dryness to render silica insoluble. The mass is then treated with strong hydrochloric acid and boiled down to a small volume. After diluting with water and filtering, the liquid is heated to 80° and saturated with hydrogen sulphide; after 12 hours, the precipitate is collected, well washed with water containing hydrogen sulphide and a few drops of hydrochloric acid, and then digested with ammonium sulphide. Any insoluble matter is freed from traces of molybdenum by fusing it in a porcelain crucible with sodium potassium carbonate and sulphur; the mass is treated with water and the filtrate added to the ammonium sulphide solution. The liquid is now heated and acidified with hydrochloric acid, which causes the precipitation of molybdenum sulphide and free sulphur. The pre-

cipitate is collected on a weighed filter, thoroughly washed with hot water, dried at 120°, and weighed. The mass is then detached from the filter, well mixed in an agate mortar, and an aliquot part is placed in a weighed boat and heated in a current of hydrogen; the molybdenum disulphide so obtained is then weighed

L. DE K.

Rapid Assay of Tungsten Ores and Residues. By HUGO BORNTAGER (*Zeit. anal. Chem.*, 1900, 39, 361—362).—Wolframite, the most common tungsten ore, contains as impurities sand, calcium, magnesium, antimony, arsenic, tin, lead, cobalt, nickel, copper, and traces of gold, with occasionally molybdenite. A gram of the finely powdered mineral is fused for an hour with 10 grams of sodium carbonate, the mass exhausted with water, and the residue ignited and weighed. By deducting this residue from 100, the percentage of tungstic acid is obtained within 5 per cent., which for rough assays is sufficiently close. For more accurate work, the aqueous extract is made up to 250 c.c., and 100 c.c. is delivered into a mixture of 15 c.c. of concentrated nitric acid and 45 c.c. of concentrated hydrochloric acid. The mixture is evaporated to dryness and extracted with a liquid containing 100 grams of ammonium chloride, 100 grams of strong hydrochloric acid, and 1000 grams of water. The insoluble matter, which contains the tungstic acid with silica and stannic oxide, is dissolved in ammonia, the solution poured into a similar acid mixture, and this liquid evaporated to dryness. The residue, washed as before, is ignited and weighed as tungstic acid. Metallic tungsten and its alloys with copper, iron, nickel, &c., should be roasted for half an hour before fusing as above, and a little nitre added to the soda.

M. J. S.

Action of Sodium Thiosulphate on Bismuthic, Ferrous, and Ferric Salts. By FRANZ FAKTOR (*Chem. Centr.*, 1900, ii, 20—21, 67; from *Pharm. Post*, 33, 301, 317).—Neutral aqueous solutions of bismuthic salts are quantitatively precipitated as trisulphide by sodium thiosulphate (? on boiling). To obtain trustworthy results in estimating bismuth by this method, the trisulphide should be moderately ignited in a current of hydrogen sulphide.

Neutral solutions of ferric salts are first coloured violet by sodium thiosulphate, but gradually assume a yellow or brownish-yellow colour, which is not altered on prolonged boiling. If, however, a little ammonia is added, a greenish-black precipitate is formed, which on continued boiling yields blackish-brown, granular, ferrous hydroxide (? ferrosiferic hydroxide). The precipitation does not seem to be complete.

Solutions of ferrous salts are not precipitated on boiling with sodium thiosulphate unless ammonium chloride and ammonia are added. The iron then gradually separates as sulphide.

L. DE K.

Electrolytic Precipitation of Antimony from its Sulpho-salt with the Application of a Diaphragm. By HERMANN OST and W. KLAPPROTH (*Zeit. angew. Chem.*, 1900, 827—829).—The authors have made an attempt to improve the electrolytic method

for the estimation of antimony by the introduction of a diaphragm in order to prevent the solution of the metal in the accumulating polysulphide.

The apparatus was composed of a Classen's platinum dish in which was suspended a basin-like diaphragm made of porous porcelain; a platinum disc in the diaphragm cell was made the anode, and the dish the cathode, and both dishes were covered with cut-out watch glasses. The experiments were made with a solution of "Schlippe's salt" containing 0.0985 gram of antimony per 10 c.c., and a solution of pure sodium sulphide containing 195 grams of this salt, equal to 200 grams of pure sodium hydroxide per litre; 10 c.c. of the antimony solution were mixed with varying amounts of sodium sulphide and then diluted to 125 c.c.

When the antimony is introduced in both anode and cathode, it is only completely precipitated in the latter; if introduced in the latter only, it is completely removed from the liquid. If introduced in the anode only, not a trace of metal is deposited at the cathode, but antimony sulphide is formed at the anode.

The completeness of the precipitation in the cathode depends slightly on the amount of sodium sulphide. If this is present in excess and when, consequently, the tension is low, all the antimony is precipitated, but in the presence of but little sodium sulphide and a high tension, a small portion of the antimony passes through the diaphragm, and is precipitated as sulphide on the anode. The metal, however, never passes from the anode to the cathode.

The other products of the electrolysis, both in the anode and cathode space, were investigated with the aid of Wehrlin's decomposition cell. The gas collecting in the cathode was proved to consist of practically pure hydrogen. At the anode, oxygen is formed, but this rarely escapes as gas, as it is at once absorbed by the sodium sulphide, forming sodium polysulphide and sodium thiosulphate.

It remains to be seen whether the use of the diaphragm is to be recommended. It presents no difficulties with antimony alone, but in the presence of tin the tension should not exceed 1 volt.

L. DE K.

Improved Absorption Apparatus for Use in the Analysis of Essential Oils. By ALFRED C. CHAPMAN and HERBERT E. BURGESS (*Analyst*, 1900, 25, 197—199).—The apparatus consists of a 250 c.c. flask with a long, narrow neck and a tubulure at the bottom through which passes a bent glass tube connected by a long piece of india-rubber to a funnel. Communication between these may be closed or established by means of a pinch-cock.

Twenty-five c.c. of the essential oil are introduced into the flask, the temperature being carefully noted. After adding a sufficiency of the absorbent, the mixture is thoroughly shaken, and the aqueous layer removed by opening the pinch-cock. A fresh quantity of absorbent may now be added, or the residual oil may be washed with either hot or cold water.

To the flask is now attached a ground, specially-constructed measuring

tube, the character of which depends on particular circumstances; it may be surrounded by a water jacket. By pouring water into the funnel and raising the india-rubber tubing, the oil is forced from the flask into the graduated tube, where its volume is then read off at the original temperature.

L. DE K.

Estimation of *m*-Cresol in Mixtures of Cresols. By FRITZ RASCHIG (*Zeit. angew. Chem.*, 1900, 759—761).—Ten grams of the sample are weighed in a small Erlenmeyer flask and mixed with 15 c.c. of sulphuric acid of sp. gr. 1.846. After being heated for an hour at 95—100°, the contents are poured into a wide-necked litre flask and rapidly cooled under a tap with circular motion to spread the compound over the sides of the flask. The Erlenmeyer flask is now quickly rinsed with 90 c.c. of nitric acid of sp. gr. 1.385, and this is poured all at once into the litre flask; the whole is thoroughly shaken for not more than 20 seconds and then put into a fume chamber. After the lapse of about 1 minute, a violent action sets in with evolution of red fumes; the clear liquid becomes turbid, oily drops of trinitro-*m*-cresol collect at the bottom, and after 5 minutes the reaction seems to be completed. After waiting 5 minutes longer, the liquid is emptied into a dish containing 40 c.c. of water and the flask is rinsed with another 40 c.c. The trinitro-*m*-cresol now solidifies to a crystalline mass, which after two hours is collected on a counterpoised filter, dried at 95—100°, and weighed. Its weight divided by 1.74 equals the amount of *m*-cresol.

The process is not applicable in the presence of large quantities of phenol.

L. DE K.

Estimation of Glycerol in Fats and Soaps. By FERDINAND JEAN (*Chem. Centr.*, 1900, ii, 293; from *Ann. Chim. anal. appl.*, 5, 211—213).—The author has applied Laborde's process for the estimation of glycerol, based on the isolation of its carbon by means of sulphuric acid (*Abstr.*, 1899, ii, 816), to the analysis of fats and soaps.

Ten grams of saponified fat or soap are dissolved in hot water and precipitated with zinc sulphate. The solution is mixed with 10 drops of sulphuric acid, evaporated to 2—3 c.c., and then treated with 6 c.c. of strong sulphuric acid at 150° as directed.

L. DE K.

Analysis of Saccharine Liquids. By GEORGES HALPHEN (*J. Pharm.*, 1900, [vi], 12, 12—14).—In Raczkowski's method of examining saccharine liquids (*Mon. Sci.*, 1896, 19), the potassium carbonate used for removing the excess of lead acetate gives rise to decomposition products of dextrin, which render the solution ultimately obtained highly absorptive of light, and thus unsuitable for polarimetric examination; the author obviates this by using calcium instead of potassium carbonate, and slightly modifying the original procedure in a few other particulars.

W. A. D.

Estimation of Sugar in Beet. By JOHANN KOVÁŘ (*Chem. Centr.*, 1900, ii, 148—149; from *Oesterr.-ung. Zeit. Zucker-Ind.*, 29, 182—209).—Three processes are in general use for the extraction

of beet for polariscopic purposes, namely, extraction with alcohol, digestion with hot alcohol of 85 per cent., and digestion with hot water.

As the result of many years' experience, the author thinks the alcoholic extraction process is the best, as fewer impurities pass into the solution. L. DE K.

[Estimation of Sugar in] Peat-meal Molasses. By RUDOLF WOX (*Chem. Centr.*, 1900, ii, 284; from *Zeit. öffentl. Chem.*, 6, 201—204).—See this vol. ii, 682.

Polarimetric Estimation of Sugar in Wine. By XAVIER ROCQUES (*Chem. Centr.*, 1900, ii, 291; from *Ann. Chim. anal. appl.*, 5, 216—219).—When polarising wine, it is necessary to first remove the alcohol, as this rapidly diminishes the rotatory power of lævulose and slightly that of dextrose; sucrose is not affected.

Formulæ are given for calculating the amount of dextrose (x) and lævulose (y) in a litre of liquid, using the polarisation (R) in circular degrees, and the gravimetric estimation of the total reducing sugars (P).

$$x = (R + mP)/(0.106 + m), \quad y = P - x.$$

$m = a_D l/v$, in which a_D is the specific rotatory of lævulose with due regard to temperature, $l = 2$ the length of the polarising tube, $v = 1000$ the volume of the liquid; m at 10° has the value 0.1916, at 15° 0.1860, at 20° 0.1748, and at 25° 0.1692. L. DE K.

Detection of Salicylic Acid in the Presence of Citric Acid. By OTTO LANGKOPF (*Chem. Centr.*, 1900, ii, 147—148; from *Pharm. Centr. H.*, 41, 335—337).—Salicylic acid cannot be detected in lemon juice by adding ferric chloride, as the citric acid interferes with the reaction. It may, however, be readily isolated by shaking the sample with a mixture of equal volumes of ether and light petroleum; ether alone should not be used as it slightly dissolves citric acid. L. DE K.

A Cause of Error in Testing for Salicylic Acid in Wines. By ANTONIO J. FERREIRA DA SILVA (*Compt. rend.*, 1900, 131, 423—424).—The Petlet-Grobert method is unsatisfactory since, with samples of pure wine, it often gives a rose or reddish-violet coloration liable to be confused with that produced by salicylic acid; the German official test, however, is always trustworthy. W. A. D.

Estimation of Uric Acid. By A. BELLOCQ (*J. Pharm.*, 1900, [vi], 12, 103—104).—To 200 c.c. of urine are added 20 c.c. of a mixture of 30 c.c. of a 1:3 solution of zinc sulphate, 30 c.c. of aqueous sodium hydroxide, and 40 c.c. of a saturated solution of sodium carbonate; complete precipitation usually occurs, a perfectly limpid liquid being obtained, but should this not happen, more of the reagent is added. The precipitate is collected, and, after draining, is easily transferred to a crucible, floating on water; 2 or 3 c.c. of hydrochloric acid saturated with uric acid are added, when crystals of uric acid rapidly separate. These are collected in a small cylindrical funnel on a wad of moistened absorbent cotton, washed with 10 c.c. of alcohol,

a second wad of cotton pressed down, and the whole transferred to a filter paper, dried, and weighed.

W. A. D.

Precipitation of Uric Acid by Barium Chloride. By ADOLF JOLLES (*Zeit. anal. Chem.*, 1900, 39, 355—357).—It was stated by Geelmuyden (*Abstr.*, 1892, 1032) that the precipitation of uric acid by barium chloride can be employed for its estimation in urine. The author admits that with pure uric acid the precipitation is fairly complete, but shows that from neutralised urine only a small fraction of the uric acid present is thrown down, whilst the precipitate contains other nitrogenous substances which Geelmuyden has mistaken for uric acid, since he confined himself to estimating the total nitrogen in the precipitate without identifying the nature of the nitrogenous substance precipitated.

M. J. S.

Composition of Milk and Milk Products. By HENRY DROOP RICHMOND (*Analyst*, 1900, 25, 225—231).—The paper contains the report on the composition of milk and allied products analysed in the laboratory of the Aylesbury Dairy Co. in 1899.

With a very few exceptions, the samples were in every respect above the legal standard; in the case of those samples which fell below 8.5 per cent. of solids not fat, it was again proved that the deficiency was solely due to lactose, and not to casein or ash.

Timpe's formula for calculating the amount of added water or of abstraction of cream, which is based on the supposed relation between proteids and fat (this vol., ii, 251), is stated to be untrustworthy and unsuitable for commercial milk-analysis.

The colour tests with *p*-phenylenediamine or *m*-phenylenediamine and amyl alcohol, proposed to distinguish between raw and heated milk, should not be implicitly depended on, and Faber's albumin test should always be applied as a check.

Analyses of butter and cream are also given; a butter prepared by an extractor supposed to increase the yield contained 20.42 per cent. of water.

L. DE K.

Umikoff's Reaction with Human Milk. By NADINA SIEBER (*Zeit. physiol. Chem.*, 1900, 30, 101—112).—Umikoff (*Trudy Wratsch. Petersburg wospitatel*, 1898) has described a reaction by which human milk can be distinguished from the milk of the cow and other vegetable feeders. If 5 c.c. of the milk are mixed with 2.5 c.c. of 10 per cent. aqueous ammonia, and the mixture kept at 60° for 15—20 minutes, a violet-red coloration is obtained. As lactation progresses, the intensity of the reaction is increased. These statements are confirmed. The substance is dialysable, and the dialysate of cow's milk gives it. The substance which gives the reaction is not lactose, as Marchetti supposed, but citric acid. Although cow's milk contains more citric acid, it also contains more calcium salts, which hinder the reaction; the dialysate contains more citric acid than calcium salts, and so gives the reaction.

W. D. H.

Composition of Danish Butter. By HARALD FABER (*Analyst*, 1900, 25, 199—201).—The samples, the analysis of which is recorded in a table, were duplicates of those taken by the Custom House offi-

cials at the port of importation every month during 1898 and 1899. The tests were limited to the determination of the Reichert-Wollny figure, the refraction in Zeiss's instrument at 45°, and the Bechi test for cotton-seed oil (margarine).

On the whole, the samples had a very high Reichert-Wollny number; in a few samples during the autumn this fell to 24.3—25.6. It has now been proved beyond dispute that the use of cotton-seed cake as cattle food may cause the butter to give a decided Bechi test, so that this does not necessarily imply any addition of margarine.

A table is given showing the average amount of water during the years 1890—1898; the highest percentage recorded is 17—18.

L. DE K.

Welmans' Phosphomolybdate Test. By P. WELMANS (*Chem. Centr.*, 1900, i, 1248—1249; from *Zeit. offentl. Chem.*, 6, 127—134, 143—148).—This is a reply to several critics who, in the author's opinion, have not consulted his original instructions.

The reagent is prepared by dissolving 20 grams of sodium phosphomolybdate in water containing 10 c.c. of 25 per cent. nitric acid, and diluting to 100 c.c. This solution should show no sign of green, and must become perfectly colourless on adding excess of ammonia. When added to pure lard, no reduction takes place, but if the sample should contain vegetable oils in sound condition a green colour is noticed. This green is really a mixture of a blue colour with the yellow colour of the reagent, and when the reduction has been very decided, the blue colour predominates. If there has been so little reduction that no green coloration is noticed, a trace of blue may be obtained by adding excess of ammonia, but no notice should be taken of such a slight reduction. The author has already stated that the reduction is undoubtedly caused by the colouring matters contained in the oils, which may be of a glucoside-like nature.

Soltzien's statement (compare following abstract), that phosphomolybdic acid even in ammoniacal solution is reduced by aldehydes, is challenged. No doubt there are a number of substances capable of reducing the reagent, but these are not likely to be met with in practice.

L. DE K.

Welmans' Reaction for the Detection of Vegetable Oils. By PAUL SOLTZIEN (*Chem. Centr.*, 1900, ii, 289; from *Zeit. offentl. Chem.*, 6, 187—190).—The colour produced on adding Welmans' reagent (preceding abstract) to a vegetable oil should be noticed after 5 minutes, as after some time all oils give the reaction. The author prefers to avoid the use of chloroform, and therefore melts the sample at a low temperature, and then adds a little of the reagent. After shaking for 5 minutes, excess of ammonia is added and the first change in colour noticed.

Butter-fat and horse-fat also give the reaction. The reagent is also reduced by furfuraldehyde and formaldehyde.

L. DE K.

Chemistry of Corn Oil [Maize Oil]. By HERMANN T. VULTE and HARRIET WINFIELD GIBSON (*J. Amer. Chem. Soc.*, 1900, 22, 453—467).—The physical and chemical constants of three samples of corn oil were

determined; (a) was a freshly prepared specimen of undoubted purity, (b) a commercial specimen, 6—7 years old, and (c) a product of the mash of distilleries, of a brown colour, and 10—12 years old. The results are summarised in the following tables:

Physical Constants.

	a.	b.	c.	Insoluble fat acids.
Specific gravity { 15°	0·9213	0·9213	0·9255	—
{ 100°	0·8711	0·8716	0·8756	0·8529
Viscosity { water (20°)	10·57	9·79	—	—
{ rape oil (20°)	73·89	70·42	—	—
Index of refraction { 15°	1·4766	1·4767	—	—
{ 20°	—	1·4761	1·4765	—
Melting-point	—	—	—	22·4°

Chemical Constants.

	a.	b.	c.	Insoluble fat acids
Ash (per cent.).....	—	0·065	0·0655	—
Acid value.....	2·25	3·70	20·65	—
Free acid (as oleic acid, per cent.)	1·128	1·851	10·386	—
Degrees of acidity.....	4·00	6·59	36·83	—
Iodine absorption (per cent.).....	118·62	119·74	113·27	120·98
Koettstorfer number	192·64	192·65	191·78	199·15
Saponification equivalent	291·22	291·21	292·55	281·72
Ether value	190·39	188·95	171·13	—
Hehner value	92·23	92·79	88·21	—
Reichert number	4·2	4·3	9·9	—
Weight of potassium hydroxide per } 100 grams of oil	0·94248	0·96492	2·22156	—
Koettstorfer number of acetic oil.	211·9	211·5	—	—
Acetyl value.....	11·49	11·12	—	—
Glycerol (per cent.).....	10·35	10·545	—	—
Unsaponifiable matter (per cent.)	1·43	1·39	—	—
Mauméné { rise in temp.	74°	75°	—	—
{ specific temp.	176·2	178·6	—	—
Bromine thermal value	21·8°	21·9°	—	21·6°
Valenta's test	80°	74°	65°	—
Livache test (gain per cent.)	5·19	5·97	—	—

in 10 days in 7 days

These observations are in each case compared with those of previous workers. The results of the application of a number of colour reactions to each sample of oil are also described. E. G.

Halphen's Colour Reaction for the Identification of Cotton Seed Oil. By P. N. RAIKOW (*Chem. Zeit.*, 1900, 24, 562—563, 583—585).—It has been proved that the active principle contained in cotton seed oil which causes the Halphen sulphur reaction is not the same substance as that which gives the Bechi silver test, as when cotton seed oil is thoroughly oxidised with potassium permanganate in the presence of cold dilute sulphuric acid, the resulting product still gives the Bechi, but no longer the Halphen, test.

Exposure of the mixture of cotton seed oil and Halphen's reagent (carbon disulphide, sulphur, and amyl alcohol) to sunlight has the same effect as heating; the colour obtained is permanent in the dark but gradually fades on prolonged exposure to light. This is not caused by the action of sunlight on the active principle itself, as cotton seed oil without any admixture of either carbon disulphide

or sulphur, after being exposed to the action of sunlight for 7 months, still gives both Bechi's and Halphen's reactions.

The conclusion finally drawn is that perhaps the active principle is an unknown unsaturated fatty acid with a side chain.

L. DE K.

Sesamé Oil. By F. UTZ (*Chem. Centr.*, 1900, ii, 293—294; from *Pharm. Ztg.*, 45, 490—491).—The author has tested African, Indian, and Levantine sesamé oil, and tabulated the results. The analysis was restricted to the sp. gr., melting point of the fatty acids, polarisation in 20 cm. tube at 15°, iodine number (Hübl-Waller), refraction of the oils at 25° and 40°, and refraction of the fatty acids at 25° and 40°; the results show that the oil has a fairly constant composition.

Colour reactions were also tried. When shaken with hydrochloric acid (Bishop's test), this turns green, the colour being strongest with Indian and weakest with Levantine oil. The latter emulsifies with the acid, and only separates when heated in the water-bath; the supernatant oil assumes a dark orange colour. The other oils do not form an emulsion with the acid, and do not darken so much. Baudouin's test (hydrochloric acid and furfuraldehyde) shows best with the African oil.

The most delicate reaction, however, is Soltsien's stannous chloride test, which allows the detection of 0.5 per cent. of sesamé oil in earthnut oil. The author also confirms the results obtained by Breinl (*Abstr.*, 1899, ii, 824) as regards the substitution of other aldehydes for furfuraldehyde.

L. DE K.

Polarimetric Estimation of Camphor in Camphorated Oil. By NORMAN LEONARD and HARRY M. SMITH (*Analyst*, 1900, 25, 202—203).—The authors have examined solutions of camphor in olive oil and its substitutes in the 200 mm. tube of a Schmidt and Haensch half-shadow polariscope, using sodium light, and find that the angular rotation is raised 1° for every per cent. of camphor. As the rotation of the oil is insignificant, it follows that the polariscope is a most convenient instrument for rapidly testing the strength of the official camphorated oil.

The results obtained practically confirm those of Chabot (*Abstr.*, 1890, 1427) and also those of Dowzard, who stated that the angular rotation per 100 mm. multiplied by 1.962 equals the percentage of camphor. The presence of the latter does not interfere with the identification of the oil by the refractometer.

L. DE K.

Influence of Dextrose on the Estimation of Urea by the Hypobromite Method. By LÉON GARNIER and LÉOPOLD MICHEL (*J. Pharm.*, 1900, [vi], 12, 53—61).—The authors justify Jacoby's statement (*Abstr.*, 1886, 104) that the addition of dextrose in the hypobromite method enhances the production of nitrogen without, however, enabling the urea to yield its full complement of gas. The dextrose is, indeed, disadvantageous, since its energetic oxidation develops heat, necessitating a delay in reading the volume of the gas, and since a small quantity of carbon dioxide is produced with the nitrogen unless a large excess of alkali be used. Moreover, the augmentation of the yield of nitrogen is not only small but indeterminate.

Quinquaud's claim (*De l'urée*, 1897, 143) to have obtained theoretical results by means of a specially concentrated hypobromite solution without employing dextrose, is shown to be fallacious; but the comparative method of estimating urea in urine as described by Yvon and by Vieillard (*Analyse des urines*) yields perfectly satisfactory results.

W. A. D.

NOTE BY ABTRACTOR.—The foregoing experiments were made with 2 per cent. solutions of urea, whereas Moreigne, in a paper apparently overlooked by the author (*Abstr.*, 1899, ii, 73), has stated that with solutions containing more than 0.5 gram in 100 c.c., an error as great as 2.5–3.0 per cent. may arise.

Detection of Foreign Colouring Matters in Preserved Tomatoes. By GEORGES HALPHEN (*Chem. Centr.*, 1900, ii, 68; from *Ann. Chim. anal. appl.*, 5, 177–179).—**Coal-tar Colours.**—The substance is mixed with sand or silica and dried; the dry mass is moistened with glacial acetic acid and then shaken with twice its volume of 90 per cent. alcohol. The filtrate is diluted with 10 times its volume of water, and boiled for 15 minutes with washed silk. If coal-tar colours are present, the silk fibres become red or rose, but if absent they only turn yellowish or brownish.

Cochineal.—The dry mass is drenched with hydrochloric acid, and after 10 minutes shaken with twice its bulk of alcohol. The filtrate is diluted with 10 vols. of water and shaken with so much amyl alcohol that about 5 c.c. of the latter collect on the surface; the aqueous layer is then drawn off. To the amyl alcohol are added 1.5 vols. of carbon disulphide and 4–5 vols. of water, and after slight shaking the bottom layer is drawn off and the aqueous top layer is filtered. In the presence of cochineal, the filtrate is more or less yellowish-red, but becomes colourless when shaken with amyl alcohol; the latter then turns green when shaken with a solution of neutral uranium acetate.

L. DE K.

[**Urinary Indican.**] By JACOB BOUMA (*Zeit. physiol. Chem.*, 1900, 30, 117–125).—Many objections are urged against the method adopted by Wang for the estimation of urinary indican.

W. D. H.

Detection of Urobilin in Urine. By TH. ROMAN and G. DELLUC (*J. Pharm.*, 1900, [vi], 12, 49–50).—The advantage of rapidity is claimed for the following method of detecting urobilin. Eight to ten drops of pure hydrochloric acid and 20 c.c. of chloroform are added to 100 c.c. of urine, and, after carefully agitating, 2 c.c. of the chloroform solution are withdrawn; 4 c.c. of a solution of 1 gram of zinc chloride in 1 litre of alcohol of 95° are then added, without mixing, when the characteristic green ring appears between the two layers. On shaking, the liquid becomes rose-coloured, and shows a green fluorescence. Certain commercial alcohols, to which no zinc salt has been added, give, with the chloroform solution, the same reaction; this is due to their having dissolved traces of zinc during manufacture or storage.

W. A. D.

General and Physical Chemistry.

Spectra of Hydrogen and of Aqueous Vapour. By JOHN TROWBRIDGE (*Phil. Mag.*, 1900, [v], 50, 338—347).—Two spectra are attributed to hydrogen, the four-line spectrum, and the “white” spectrum consisting of a great number of lines. The author has studied the spectra with very powerful condenser discharges, employing a battery of twenty thousand Planté cells, and is of the opinion that the “white” spectrum only is a true hydrogen spectrum, and that the four-line spectrum is due to water vapour. In spite of all precautions to ensure dryness of the gas in glass vessels, it cannot be considered as dry when a condenser discharge is passed, since aqueous vapour is liberated from the glass, and with the powerful discharges employed essentially the same spectrum is obtained with hydrogen, rarefied air, or nitrogen. Aqueous vapour is therefore considered to be present in the solar atmosphere. Conclusions regarding the pressure and temperature of hydrogen in stars deduced from laboratory experiments in glass vessels are misleading, since conditions of electrical dissociation, aqueous vapour, &c., affect the nature of the spectrum more than pressure and temperature. L. M. J.

Influence of Slight Impurity on the Spectrum of a Gas. II. By PERCIVAL LEWIS (*Ann. Phys.*, 1900, [iv], 2, 447—458. Compare this vol., ii, 1).—The influence of a trace of mercury vapour on the spectrum of hydrogen has again been determined, this time with internal electrodes of iron; the intensity of the hydrogen lines is considerably diminished. The spectrum of nitrogen mixed with a trace of mercury, oxygen, or water vapour has been examined, and found to be less intense than that of the pure gas. The intensity of the bands in pure nitrogen reaches a maximum at a pressure of 3.5 mm. Sulphur and iodine vapour are without influence on the intensity of the nitrogen bands. The author considers that in spectroscopic investigations more account should be taken of the influence of slight impurity. J. C. P.

Lamps for Spectra. I. By ERNST BECKMANN (*Zeit. physikal. Chem.*, 1900, 34, 593—611).—The author, after discussing the various methods of colouring non-luminous flames, describes an apparatus whereby a fine spray of the colouring substance may be introduced into a flame. The tube of a burner is divided into two branches, which are bent round so that the outlets face each other. Below the point where the two jets meet, there is placed a small vessel containing a solution of the substance under examination. In this solution there is a spray-producer, consisting of a closed porous porcelain tube. This tube, which is connected with a reservoir of compressed air, allows a fine stream of the air to pass through and carry with it enough of the solution to impart a steady colour to the flame above. The permeability of the porcelain tube is increased, and the flame

colour rendered more intense, by impregnating the former with alcohol or some other organic liquid. J. C. P.

Fluorescence and Afterglow accompanying an Electric Discharge in Nitrogen. By PERCIVAL LEWIS (*Ann. Phys.*, 1900, [iv], 2, 459—468).—These phenomena are fully described by the author, and attributed to minute traces of oxygen present in the nitrogen. This oxygen probably is liberated by the discharge from a small quantity of water vapour persistently held by the glass. When the discharge tube is dried by heating sodium in it, neither fluorescence nor afterglow is observed. J. C. P.

Phosphorescence of Inorganic Substances. By EUGEN GOLDSTEIN (*Sitzungsber. K. Preuss. Akad. Wiss.*, 1900, 818—828).—Phosphorescence can be very advantageously detected by means of a form of apparatus in which the powdered substance falls from end to end of an exhausted tube, and is illuminated by cathode rays at one part of it; phosphorescent substances show a streak of coloured light, whilst other substances are only luminous in the path of the rays. The irregular results which have been usually obtained are due to impurities; salts of Li, Na, K, Rb, Cs, Ca, Sr, Ba, Al, Zr, Mg, Be, Zn, and Cd, which for the most part form colourless oxides, all show a blue to violet fluorescence, but minute traces of Cu, Cr, Mn, U, Ni, Co, Pb, Ce, La, Y, Er, Pr, or Nd suffice to produce a strong fluorescence which often entirely masks the blue fluorescence of the pure substance. T. M. L.

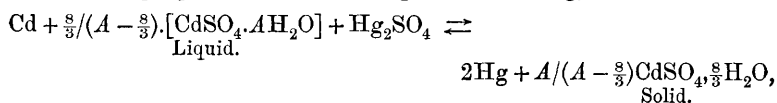
Action on Photographic Plates of Minerals containing Uranium and Thorium. By AFANASSÉEFF (*J. Russ. Phys. Chem. Soc.*, 1900, 32, ii, 103—106).—Fifty-one minerals were examined with regard to their power of emitting rays capable of affecting a photographic plate. In general, the presence in a mineral of a large percentage of uranium or thorium corresponds with a relatively intense photographic action. The fact that laranskite, which contains no uranium or thorium, produces an impression on a photographic plate, is explained by the presence in it either of some other mineral containing one of these metals or of a new element. T. H. P.

Meta-stable Character of the Weston Cadmium Element and its Uselessness as a Standard Cell. By ERNST COHEN (*Zeit. physikal. Chem.*, 1900, 34, 621—631).—Cadmium sulphate, $\text{CdSO}_4 \cdot \frac{8}{3} \text{H}_2\text{O}$, can exist in two different modifications below 15° . A cadmium amalgam with 14.3 per cent. of cadmium can exist in two different modifications below 23° . At 0° , the difference of potential between the two modifications of the cadmium amalgam amounts to 5 millivolts. It appears that the Weston cell studied in the Reichsanstalt is below 23° a meta-stable system, which may spontaneously change into a stable condition. As this change is accompanied by an appreciable alteration in the E.M.F., the Weston cells are useless as standards. The temperature formula given by Jaeger and Wachsmuth (*Abstr.*, 1897, ii, 86) applies between 0° and 23° to the meta-stable Weston cell, above 23° to the stable form of the same.

The author hints that probably similar results will be obtained in regard to the stability of the Clark cell. J. C. P.

The Weston Cell. By WILHELM JAEGER and ST. LINDECK (*Zeit. physikal. Chem.*, 1900, **35**, 98—99).—Cohen (preceding abstract) has stated that below 23° the Weston cell is in a meta-stable state and is hence unsuitable for a normal element. The authors dissent from his views and point out that the concentration of the amalgam employed by Cohen (14·3) is considerably greater than that of the normal Weston cell (12·7). L. M. J.

Thermodynamics of Normal Cells. II. By ERNST COHEN (*Zeit. physikal. Chem.*, 1900, **34**, 612—620).—The calculations made in the previous paper (this vol., ii, 520) relative to the Clark cell were based on measurements made with the system $\text{Hg} \mid \text{Hg}_2\text{SO}_4$ —saturated zinc sulphate solution \mid zinc amalgam. No error was thereby introduced, since zinc and zinc amalgam show the same potential difference in a zinc sulphate solution, provided the amalgam contains more than 2 per cent. of zinc. With the cadmium of the Weston cell, which is dealt with in the present paper, the case is different; the 14·3 per cent. cadmium amalgam used in Jaeger and Wachsmuth's work (*Abstr.*, 1897, ii, 86) shows an electromotive behaviour different from that of pure cadmium. Taking account of this, the essential changes that take place in the Weston cell are represented by the following equations: $\text{Cd} - \text{amalgam} \rightleftharpoons \text{Cd} + \text{Hg}$, and



where A is the number of water molecules present for every one of cadmium sulphate in the saturated solution. On this basis, E_c , the total heat effect accompanying the passage of 2×96540 coulombs through the cell, is calculated to be 47286 cal., whilst the electrical measurements of Jaeger and Wachsmuth lead to the value 47880 cal. J. C. P.

An Application of Poynting's Theorem. By GUSTAV MIE (*Zeit. physikal. Chem.*, 1900, **34**, 522—528).—A mathematical paper not suitable for abstraction. J. C. P.

Quantitative Lecture Experiments on Electrochemistry. By W. LASH. MILLER and FRANK B. KENRICK (*J. Physical Chem.*, 1900, **4**, 599—618).—The authors describe a very ingenious instrument for use on a lecture table which is capable of marking the necessary changes of resistance in a Wheatstone bridge and of indicating to a class the resistance required. The principle of the method is the following. The needle of a dead beat galvanometer of the D'Arsonval pattern, when displaced from its zero position, completes a relay circuit and by means of suitable mechanism causes a rheostat to turn and alter the resistance, the direction being dependent on the side to which the needle moves. This rheostat is provided with a dial and pointer, which indicate the resistance. When the equilibrium is reached and the

needle returns to zero, contact is broken and the motion of the rheostat ceases. The authors describe how, by means of this instrument, various electrolytic experiments may be shown to a class, as, for example, the proof of Ostwald's law, preparation of isohydric solutions, measurements of E.M.F.s, and of polarisation, &c. L. M. J.

Relations between Polarisation and Current Density in Solid and Fused Salts. By ALBERT GÖCKEL (*Zeit. physikal. Chem.*, 1900, **34**, 529—558).—A number of experiments made with lead chloride, bromide, and iodide, cadmium iodide and bismuth bromide, at temperatures both above and below their melting points, show a rapid increase of the polarisation with the current density. The chief factors to be taken into account are the absorption of the liberated gases by the electrodes, and the solution and diffusion of these gases in the electrolyte. On the supposition that the concentration of the gas absorbed in the anode is proportional to the potential difference between the electrodes (compare Jahn and Schönrock, *Abstr.*, 1895, ii, 198), a formula is deduced giving the polarisation in terms of the current density. This formula agrees closely with the experimentally determined relation of polarisation and current density, except for high values of the latter and at temperatures much above the melting point of the salt. Under these conditions, the values of the polarisation approach a maximum, and a hyperbolic curve must be substituted for the logarithmic one. J. C. P.

Difference of Potential between a Solid Salt and its Solution. By A. CAMPETTI (*Atti Real. Accad. Lincei*, 1900, [v], **9**, ii, 27—31).—By measuring the E.M.F. of a cell of the type $\text{Hg} | \text{L}_1 | \text{salt} | \text{L}_2 | \text{Hg}$, where L_1 and L_2 are solutions of different concentrations of the solid salt in contact with them, it is found that a difference of potential exists between a solid salt and its non-saturated solution, the order of magnitude and sign being the same as those of the potential difference existing between a concentrated and a dilute solution of the same salt. T. H. P.

Electromotive Efficiency of the Elementary Gases. I. By EMIL BOSE (*Zeit. physikal. Chem.*, 1900, **34**, 701—760).—A general review of the work done on gas cells, and a discussion of their theory. The chief problems treated by the author are: (1) In what condition are the gases present in the electrode? (2) What is the part played by the electrode itself? (3) How do the metallic electrodes transmit the electromotive efficiency of the gases? (4) How far is agreement attained between measurements made with the same gas and electrolyte, but with different electrodes?

The conclusions of the paper are as follows. The electromotive efficiency of the elementary gases is determined by their solubility in the electrodes. The gases in the electrodes, on account of the high dissociating power of the latter, are to be regarded as wholly or partly dissociated into single atoms; the ions of an electromotively active substance are already present in the electrode. The electrolytic solution pressure is the product of the osmotic pressure of these ions and a factor which is a constant for each solvent, and termed by the

author the electrolytic partition coefficient. The saturation of the electrode with a gas is an extremely slow diffusion process. Grove's gas battery is reversible, but its E.M.F. with the gases under atmospheric pressure has certainly a higher value than that usually given. In the acid hydrogen-oxygen cell, the water is formed at the oxygen electrode, in the alkali hydrogen-oxygen cell at the hydrogen electrode. The second electrolytic decomposition point of water corresponds with a non-reversible process.

J. C. P.

Electromotive Behaviour of Substances with several Stages of Oxidation. I. By ROBERT LUTHER [with D. R. WILSON] (*Zeit. physikal. Chem.*, 1900, **34**, 488—494).—On thermodynamical grounds, the same amount of work must be required to raise a substance from its lowest (*L*) stage of oxidation to its highest (*H*), whether this is done directly or through an intermediate (*I*) oxidation stage; thus $A_{L-H} = A_{L-I} + A_{I-H}$, where *A* is the change in the free energy. Application of this general theorem to the oxidation of copper from the metallic to the cupric stage leads to the relation: $2\Pi_{Cu} \rightarrow Cu \cdot \cdot = \Pi_{Cu} + Cl' \rightarrow CuCl + \Pi_{CuCl} \rightarrow Cu \cdot \cdot + Cl'$; a similar relation is deduced when bromine is substituted for chlorine. Under the supposition that the E.M.F. between metal and electrolyte depends on the concentration of the particular metallic ion, the deductions from the theory were confirmed experimentally in both the above cases.

J. C. P.

Passivity of the Metals. By WILHELM HITTORF (*Zeit. physikal. Chem.*, 1900, **34**, 385—402).—The author's work on the electromotive behaviour of chromium (Abstr., 1898, ii, 363; 1900, ii, 127) has suggested that the passive or inactive condition of iron may not be due to a superficial layer of oxide, as generally supposed. When in the combination $Fe | NaNO_3, H_2CrO_4 | Pt$, the circuit is completed by dipping the iron in the salt solution, the E.M.F. gradually falls from 1.83 to 0.1 volt; the iron becomes quite passive, retains its metallic lustre, and is not attacked, however long the cell is short-circuited. The metal gradually returns to its active condition when it is washed, dried, and allowed to lie in the air, or when the circuit is opened. These facts show that the passive condition of iron cannot be due to a film of oxide. Similar results are obtained when the sodium nitrate in the cell is replaced by other oxy-salts or by a soluble cyanide. The concentration of the electrolyte in which the iron is immersed has but little influence on the phenomenon. The longer the cell has been short-circuited, the longer is the iron in recovering its activity.

Iron becomes passive still more readily when it is made the anode with a stronger current. If the external E.M.F. is high enough to decompose the electrolyte, bubbles of oxygen are liberated at the iron anode, the latter behaving like a noble metal; at the same time, the surrounding liquid becomes acid. Iron that has become passive loses its passivity at once when it acts as a cathode. Immersion in strong nitric acid induces passivity, but the passivity lasts only as long as the immersion; to nitric acid of sp. gr. 1.35, iron is indifferent only when in contact with an electronegative conductor, such as platinum or gold; the passivity caused in this way endures after the contact is

broken. Potassium and sodium hydroxides render iron passive under the same conditions as the salts of the oxy-acids. When the iron in the cell $\text{Fe} \mid \text{NaNO}_3, \text{H}_2\text{CrO}_4 \mid \text{Pt}$ has been tarnished by heat, the E.M.F. is the same as when freshly polished iron is used, a further fact opposed to the view that passivity is due to superficial oxidation.

When nickel takes the place of iron in the cell just described, the E.M.F. likewise decreases, so that nickel also can assume the passive condition. Cobalt also is capable of passivity, but to a less extent than nickel.

The author looks on the molecules of a passive metal as being in a certain state of tension, which passes away when the metal is left to itself. J. C. P.

Oettel's Gasometric Method. By ANDRÉ BROCHET (*Bull. Soc. Chim.*, 1900, [iii], 23, 724—726).—A concise explanation of the method devised by Oettel for the continuous study of electrolysis. The volumes of hydrogen and oxygen evolved at the cathode and anode respectively, are compared with the volumes of these gases yielded by a gas voltameter placed in circuit with the electrolytic cell. N. L.

Accessory Reactions in Electrolysis. By ANDRÉ BROCHET (*Bull. Soc. Chim.*, 1900, [iii], 23, 736—740).—In the electrolysis of concentrated solutions of sodium hypochlorite, more of this salt is decomposed, and more chlorate is produced, than is required by Faraday's law. This result is explained by the fact that the liquid in the immediate neighbourhood of the anode is always acid and that the hypochlorous acid thus liberated in concentrated solution is partially transformed into chloric acid by auto-oxidation (this vol., ii, 276). The decomposition is quite independent of the electrolytic action, although indirectly caused thereby, and may fitly be termed an "accessory" reaction. N. L.

Researches on Electrolytic Reduction. By WALTHER LÖB (*Zeit. physikal. Chem.*, 1900, 34, 641—668. Compare Abstr., 1899, i, 122).—The main portion of this paper has already been abstracted (this vol. i, 697). In addition, the author replies to Haber's criticism of his views, and holds that no objection can be made to the assumption that the work of reduction in alkaline solution is effected by the sodium ions. A large number of chemical processes support this view. J. C. P.

Electrolytic Solution Pressure. Reply to Lehfeldt. By FRIEDRICH KRÜGER (*Zeit. physikal. Chem.*, 1900, 35, 18—22).—Many of the numerical data given by Lehfeldt in his criticism of the theory of solution pressure (this vol., ii, 62) are incorrect, notably the statement that for the formation of the double layer 1.27 grams of zinc per square cm. must pass into solution; the author calculates that this value should be 3×10^{-9} .

WALTHER NERNST in a footnote to the paper, also replies to Lehfeldt's statement that the theory of concentration chains was developed on an insufficient experimental basis. L. M. J.

Degree of Dissociation and Dissociation Equilibrium in the case of Highly Dissociated Electrolytes. By HANS JAHN (*Zeit. physikal. Chem.*, 1900, 35, 1—10).—The author has previously pointed out that the cause of the apparent divergences from Ostwald's law probably lies in the variation of ionic velocities (this vol., ii, 522). By E.M.F. observations, the ratio of the ionic concentrations of two solutions can be found, and, assuming Ostwald's law, the actual concentration may also be determined. The author calculates in this manner the ionic concentration of a dilute solution of potassium chloride from E.M.F. observation with six other more concentrated solutions; the values obtained from the last five solutions only vary between 0.001638 and 0.001642. Similar results were obtained for hydrochloric acid and sodium chloride. Assuming the value so obtained for the most dilute solution, the ionic concentrations of the stronger solutions were calculated and are found to agree well with the values calculated by the dilution law. By comparing these values with those obtained by conductivity experiments, the ionic velocities are determined and are found in all cases to decrease with dilution. There is hence no reason for doubting the validity of Ostwald's dilution law, even for strong electrolytes.

L. M. J.

Magnetic Force of the Atoms. By ROBERT LANG (*Ann. Phys.*, 1900, [iv], 2, 483—494).—A paper mainly physical in character. The author suggests that free valencies are responsible for the atomic magnetism, and points out that for cobalt, nickel, iron, and manganese the atomic magnetisms and the number of free valencies run parallel. It is also noted that the two conditions for the appearance of paramagnetism, namely, (1), a minimum atomic volume, (2) free valencies, are fulfilled in the case of oxygen. The author's view of the connection between free valency and atomic magnetism would explain the rule found by Meyer (this vol., ii, 7), that the molecular magnetism of paramagnetic compounds is less than the sum of the atomic magnetisms of the components.

J. C. P.

Has Magnetism an Influence on Chemical Reactions? By ALEXANDRE DE HEMPTINNE (*Zeit. physikal. Chem.*, 1900, 34, 669—682).—Although, according to theory, magnetism must have an influence on chemical equilibrium and reaction velocity, yet this influence is too small to be of any practical consequence. The electrical conductivity of a solution, the catalytic action of acids, the inversion of cane sugar, and the velocity of combination of hydrogen and chlorine are found to be unchanged in a magnetic field.

J. C. P.

Magnetic Behaviour of Alcohols. By GG. HEINRICH (*Chem. Centr.*, 1900, ii, 156; from *Sitzungsber. Bayr. Akad. Wiss.*, 1900, 33—36).—All alcohols exhibit diamagnetism. For one and the same alcohol the product of kM , the molecular magnetism, and H , the field strength is constant. This product kMH is different for different alcohols, and is not a purely additive but a constitutive constant. It has the following values: methyl alcohol, -0.185 ; ethyl alcohol -0.296 ; n -propyl alcohol -0.392 ; isopropyl alcohol -0.409 ; n -butyl alcohol -0.520 ; isobutyl alcohol -0.541 ; trimethylcarbinol -0.482 ; isomethyl alcohol -0.599 ; dimethylethylcarbinol -0.563 .

J. C. P.

Magnetic Susceptibility of Aromatic Organic Substances.

By HUGO FREITAG (*Chem. Centr.*, 1900, ii, 156; from *Sitzungsber. Bayr. Akad. Wiss.*, 1900, 36).—The same general relations hold as for the alcohols investigated by Heinrich (preceding abstract). The product kMH has the following values: *o*-xylene - 0.734; *m*-xylene - 0.718; *p*-xylene - 0.685; ethylbenzene - 0.675; ψ -cumene - 0.823; mesitylene - 0.773. J. C. P.

Relation between Heat of Solution and Solubility of Electrolytes. By J. J. VAN LAAR (*Zeit. physikal. Chem.*, 1900, 35, 11—17).—The author's and van't Hoff's formulæ connecting the heat of solution and solubility of electrolytes contain certain integration difficulties leading to errors which are not negligible. The author modifies his formula so as to make these smaller, and shows that it leads to better results. L. M. J.

Continuous Change and Thermodynamics. VI. By PIERRE DUHEM. (*Zeit. physikal. Chem.*, 1900, 34, 312—377).—A continuation of the author's previous papers on this subject (*Abstr.*, 1897, ii, 439; 1898, ii, 132; this vol., ii, 524), in which it is shown that the change from yellow to red phosphorus is probably an example of the same form of slow change as that of monoclinic to rhombic sulphur (*Abstr.*, 1897, ii, 439). The hardening, tempering, scorching, and forging of metals are also considered, the changes being regarded as of the nature of hysteresis and the equations previously deduced are applied. L. M. J.

Diminution of Vapour Pressure and Elevation of Boiling Point of Dilute Solutions. By A. SMITS (*Proc. K. Akad. Wetensch. Amsterdam*, 1900, 2, 635—640. Compare this vol., ii, 389).—Making use of the apparatus formerly described (*loc. cit.*), measurements have been made of the elevation of boiling point of solutions of varying concentration of potassium chloride and nitrate, and sodium chloride, and, in the case of the last salt, of the diminution of vapour pressure also. The following table gives the concentrations of the various solutions corresponding with an increase of the boiling point of water of 1°, 2°, &c.

Increase in boiling point.	Grams of salt per 100 grams water.		
	Sodium chloride.	Potassium chloride.	Potassium nitrate.
1°	7.7	9.0	12.2
2	13.4	17.1	26.4
3	18.3	24.5	42.2
4	23.1	31.4	59.6
5	27.1	37.8	78.3

Thus, in the case of potassium nitrate, the fact, already noticed for dilute solutions, that the concentration increases more rapidly than the elevation of boiling point, also holds for concentrated solutions. This is also true for dilute solutions of sodium and potassium chlorides, but with concentrations greater than 0.5 gram-mol. per 1000 grams of water the ratio of concentration to elevation of boiling point decreases. T. H. P.

Vapour Pressure of a Series of Benzene Compounds. By BENEDIKT WORINGER (*Zeit. physikal. Chem.*, 1900, **34**, 257—289).—The vapour pressure curves were determined by the statical method for benzene, hexylene, hexane, toluene, octane, ethylbenzene, *p*-xylene, *m*-xylene, *o*-xylene, propylbenzene, isopropylbenzene, decane (diamyl), isobutylbenzene, ψ -cumene, cymene, and mesitylene; expressions of the form $p = ae^{-b/\theta} \cdot \theta^{c+d \log \theta}$ are used to represent the curves, θ being the absolute temperature and a, b, c, d being constants. The vapour pressure curve of mesitylene is noticeable, as owing to the slow temperature increase it cuts those of most of the other compounds. From the results the author enunciates eleven laws, for which the original must be consulted.

L. M. J.

Cryoscopic and Ebullioscopic Researches. By ANGELO BATELLI and A. STEFANINI (*Ann. Chim. Phys.*, 1900, [vii], **20**, 64—125).—The authors consider very fully the various errors of experiment in cryoscopic observations, but add nothing to what has already been published by Wildermann (this vol., ii, 131); they also discuss the results of Loomis, Jones, Abegg, Wildermann, Ponsot, and Raoult. The apparatus employed by the authors themselves is described, and the results are given of their observations with solutions of tartar emetic and sucrose. For the latter, the value 2.02 was obtained for the molecular depression in a *N*/1000 solution, but for solutions of 2.2 *N*/1000 to 4.2 *N*/100 the values only vary between 1.83 and 1.88, so the conclusion is drawn that within the limits of experimental error the molecular depression is constant, and equal to the calculated value 1.87. An apparatus for the determination of boiling points is also described, by means of which the molecular weight of tartar emetic was found, the values varying from 287 to 329.

L. M. J.

Calculations in connection with the Equations of Condition for Liquids. I. Determination of the Constants a and b of van der Waals' Equation. By PHILLIPE A. GUYE and L. FRIDERICH (*Chem. Centr.*, 1900, ii, 156; from *Arch. Sci. phys. nat. Genève*, [iv], **9**, 505—536).—The authors consider that too little use has been made of the experimental data available for this purpose, and calculate the value of the constants for a number of substances, as summed up in the following table:

Substance.	T_c .	P_c .	a .	b .	Substance.	T_c .	P_c .	a .	b .
			0.0	0.00				0.0	0.00
NH ₃	403	114	82	162	HCO ₂ Me ...	487	59.3	236	384
NH ₂ Me....	428	72	148	276	HCO ₂ Et ...	508	46.8	330	511
NHMe ₂	436	56	198	362	CH ₃ •CO ₂ Me	507	46.3	515	514
NH ₂ Et....	450	66	178	316	CH ₃ •CO ₂ Et	523	38.0	438	654
NMe ₃	433.5	41	271	495	C ₆ H ₅ Cl.....	634	45	427	596
NH ₂ Pr....	491	50	286	460	C ₆ H ₅	562	49	390	569
NHEt ₂	489	40	359	576	C ₆ H ₅ Me ...	594	42	524	684
NHPr ₂	550	31	611	855	H ₂ O	637	195	1204	147
NEt ₃	532	30	589	852	HCl	325	86	704	174
OMe ₂	403	57	165	328	SO ₂	428	79	1345	251

In the course of these calculations the authors find empirically a numerical relation between b , the critical pressure P_c , and the critical temperature T_c .

J. C. P.

A New Coal Calorimeter. By SAMUEL W. PARR (*J. Amer. Chem. Soc.*, 1900, 22, 646—652).—The apparatus differs from those usually employed in the fact that no gaseous oxygen is required, the coal being burned by means of sodium dioxide; the carbon dioxide and water produced are absorbed by the sodium oxide formed.

One gram of the sample, dried at 105°, is mixed with 17 grams of sodium dioxide, the mixture is put into a cartridge which is placed into an insulated vessel containing a certain volume of water of known temperature. The charge is fired by means of a red hot copper wire, the increase in temperature is noticed, and the usual calculation made. For exact particulars of the construction of the apparatus and the cartridge, the illustrations of the original paper should be consulted.

An allowance of 27 per cent. of the total indicated heat must be made on account of the heat developed in the combination of the carbon dioxide and the water with the chemical employed. An allowance must also be made for the use of the hot copper wire; the average of many determinations on various lengths up to 2 inches established a fairly uniform factor of 0.012° per half-inch of No. 12 copper wire.

L. DE K.

Heat of Formation of Alloys. By J. B. TAYLER (*Phil. Mag.*, 1900, [v], 50, 37—43).—The heats of formation of a number of alloys were determined by measuring the heat of solution in mercury of the alloy and of the mixed metals, the assumption being made that the solutions are identical. It was thought that combination only took place for a very small proportion of the mixed metals, and that the best results would therefore be obtained when one metal is present in great excess, but the results showed that in this case far greater values for the heat of formation are obtained.

L. M. J.

Want of Uniformity in the Action of Copper-Zinc Alloys on Nitric Acid. By JOHN H. GLADSTONE (*Phil. Mag.*, 1900, [v], 50, 231—237).—The heats of formation of copper-zinc alloys have been determined from observations on the heat of dissolution of alloys and mixtures in nitric acid. These are shown to be untrustworthy, inasmuch as the products of the reaction are not similar in the two cases. By comparison of the heats of dissolutions of a few alloys rich in copper, for which, however, the products are practically identical, the author finds that the heat evolved is less than would be expected, and considers the deficit must be regarded as due to the heat of formation of the alloy. Further experiments are, however, desirable, with solvents the action of which is simpler than that of nitric acid (compare preceding abstract).

L. M. J.

Steam and Brines. By JOHN Y. BUCHANAN (*Trans. Roy. Soc. Edin.*, 1898, 39, 529—573).—The temperatures of boiling mixtures of steam and numerous salts have been determined under different pressures, the method followed being to blow steam through the coarsely powdered salt. The boiling temperature of the mixture is constant so long as there is an abundant supply of steam and salt.

The experiments were continued after all the salt was dissolved, the weight of steam condensed and the temperature of the liquid being observed at intervals; in this way, the concentrations and boiling temperatures of salt solutions of different strengths were determined.

The most complete series of experiments were those made with sodium chloride. In these, the atmospheric pressure varied from 550—772 mm., and the temperature of saturated steam from 91·2—100·44°, the corresponding temperatures of the boiling saturated solution being 99·3° and 108·98°. The ratio of the atmospheric pressure to the vapour tension of water at the temperature of the boiling mixture is practically constant, and equal to 0·7435. The other salts experimented with were potassium, ammonium and barium chlorides, potassium chlorate, sodium, barium, strontium and lead nitrates, potassium and ammonium sulphates. For these salts, the ratio $(p - P)/p$, where P is the atmospheric pressure, and p is the vapour tension of water at the temperature of the boiling mixture, decreases with falling pressure; this depends chiefly, if not entirely, on the diminished solubility of the salt at the lower temperature.

When $t - T$ is the difference between the boiling point of a solution and the boiling point of water at the same time and place, and W is the weight of steam condensed between the beginning of the experiment and the time when the difference of boiling points is $t - T$, it is found that $W(t - T)$ for some salts is nearly constant. For sodium and potassium chlorides, the values of $W(t - T)$ diminish very considerably as W increases.

One or two solubilities at the boiling point t of the saturated solution may be noted; the quantity of salt taken in each case is 0·2 gram-molecule.

	NaCl.	KCl.	BaCl ₂ .	(NH ₄) ₂ SO ₄ .
t	108·98°	108·94°	104·46°	107·03°
a	29·9	25·9	64·0	25·0

a is the weight of steam condensed for complete solution.

J. C. P.

The Law of Cailletet and Mathias and the Critical Density.
By SYDNEY YOUNG (*Phil. Mag.*, 1900, [v], 50, 291—305).—By the examination of the known data in the case of about 30 different compounds, the author tests the validity of the law of Cailletet and Mathias which states that the mean of the densities of liquid and saturated vapour of any stable substance is a rectilinear function of the temperature. The law is not found to be absolutely true, but is a very close approximation, the values, when plotted, forming a curve the curvature of which decreases the more nearly the ratio of the actual to the theoretical critical density approaches the theoretical value 3·77. This is well seen in the case of *n*-pentane, for which the ratio is 3·765 and for which the law holds accurately. The curvature is also found to be in opposite directions according as the ratio is greater or less than 3·77. The ratio aT_c/D_c , where a is the temperature coefficient of the mean density, appears to have a normal value of 0·93 and varies in the same sense as the above ratio. The curvature of the mean density curve is as a rule so slight that the critical density may be

calculated if the extrapolation is small, but errors of 5 or 6 per cent. may occur if the calculation is made from the mean densities at temperatures below the boiling point.

L. M. J.

Velocity of Solidification and Viscosity of Supercooled Liquids. By HAROLD A. WILSON (*Phil. Mag.*, 1900, [v], 50, 238—250).—The velocity of solidification of a supercooled liquid increases with the supercooling until a maximum constant value is reached, after which it may decrease; various explanations, but none entirely satisfactory, have been given for this (Tammann, *Abstr.*, 1898, ii, 425). The author, starting with the supposition that solidification is due to the difference of internal pressure between liquid and solid at the surface of separation and the consequent forcing of liquid molecules into the solid, deduces the expression $v = Cs/V$, where v is the velocity of solidification, c a constant, s the supercooling, and V the viscosity of the liquid. The temperature at the surface of separation of solid and liquid is not equal to that of the main bulk, and was determined in the case of salol by means of a small thermo-couple, and the values of the supercooling were corrected. The viscosity was also determined, and the value of C being deduced from the experiments the values of v were calculated for the whole series and found to agree well with the observed values. Concordant values were also obtained for benzoic anhydride, benzophenone and azobenzene, although the corrections for the overcooling were not found, and the author's formula appears to be well justified.

L. M. J.

Extent to which the Interaction of Ionic Charges diminishes the Osmotic Pressure. By VL. VON TÜRIN (*Zeit. physikal. Chem.*, 1900, 34, 403—408).—A mathematical paper not suitable for abstraction.

J. C. P.

A Model to Show Ionic Mobility. By FRIEDRICH KOHLRAUSCH (*Zeit. physikal. Chem.*, 1900, 34, 559—560).—Small metallic cylinders representing various ions have attached to them cords passing over grooved wheels, and move up and down in channels cut in the face of an upright wooden board. The size of the wheels is so adjusted that the velocities of the cylinders upwards and downwards are in the ratio of their ionic velocities.

J. C. P.

Supposed Isomerism of Red and Yellow Mercuric Oxide, and the Surface Tension of Solid Bodies. By WILHELM OSTWALD (*Zeit. physikal. Chem.*, 1900, 34, 495—503).—The difference of potential found by Cohen (this vol., ii, 184, 381) is not necessarily in conflict with the author's view that the only distinction between red and yellow mercuric oxide lies in the size of the grains. Such a difference in grain would mean a difference in solubility, and this again would cause a difference in potential. The author describes how the red oxide by mere rubbing up in a mortar takes on the colour of the yellow oxide. That the fine precipitated yellow oxide is more soluble than the larger grained red oxide was shown by shaking each with normal potassium bromide solution until equilibrium was established (compare Bersch, *Abstr.*, 1891, 1413). As the red oxide was powdered its solubility gradually approached that of the yellow oxide.

The author regards this case as illustrating the influence of surface tension on chemical equilibrium, and describes further experiments in which a difference in grain size was found to cause a difference in solubility. When two corresponding values of the grain size and solubility are known, a formula may be obtained for the surface tension between solids and their saturated solutions. J. C. P.

Composition of the Surface Layers of Aqueous Solutions. By JAN VON ZAWIDZKI (*Zeit. physikal. Chem.*, 1900, 35, 77—80).—A small quantity of saponin was mixed with solutions of acids, and a current of air, previously passed through a similar solution (without the saponin), was drawn through the acid causing it to froth up, this froth being collected and condensed in a second vessel. The concentrations of acid in the solution and froth were then determined. With acetic and hydrochloric acids, an increase of 0.4 and 0.8 per cent. respectively was found; this could not be an effect of volatility, as, apart from the precautions observed, the variation due to this cause should be in opposite senses for the two acids. The results hence confirm theoretical deductions that the concentration is greater in the surface layers. L. M. J.

Formation of Salts in Alcoholic Solutions. By SIMEON TANATAR and BORIS KLIMENKO (*Zeit. physikal. Chem.*, 1900, 35, 94—95).—The authors' previous experiments were extended to propionic, caprylic, hippuric, acetic, and chloroacetic acids (see Abstr., 1898, ii, 563). The heat of neutralisation by ammonia was in all cases greater than that by potassium hydroxide, and the values are not in the same order. For potassium hydroxide, the values lie between 7.4 and 8.9, and for ammonia between 11.5 and 14.4, so that they differ considerably from the values in aqueous solutions. The authors intend to further determine the dependence of the values on the state of ionisation. L. M. J.

Colloidal Metallic Solutions. By K. STOECKL and LUDWIG VANINO (*Zeit. physikal. Chem.*, 1900, 34, 378—379).—A controversial paper in which the authors defend their views concerning the nature of colloidal solutions (this vol., ii, 11). L. M. J.

Flocculation of Turbid Media. By WALTHER SPRING (*Rec. Trav. Chim.*, 1900, 19, 204—235).—This paper commences with an historical summary of the researches of previous observers on liquids rendered turbid by the presence of solid substances in a minute state of division (pseudo-solutions), and a bibliography of the subject is given in an appendix. Details are then given of the author's own experiments, the results of which are summarised as follows.

Solutions of salts which, like those of polyvalent metals, cannot be obtained in an optically transparent condition (Abstr., 1899, ii, 537) bring about the flocculation of turbid liquids much more readily than solutions of any other salts. This result is due partly to the agglutinative power of the metallic hydroxides formed by the hydrolysing action of the water, and partly to the flocculating action

of the acids simultaneously produced. The extent of the flocculation caused by hydroxides is closely connected with their chemical and physical character as well as with the nature of the turbidity. The behaviour of the turbidity towards salt solutions somewhat resembles that of a membrane, the acid formed by the hydrolysis of the salt traversing the liquid by diffusion whilst the metallic hydroxide is precipitated with the substance causing the turbidity. The persistence of very fine turbidities bears a relation to the Brownian motion. In consequence of this motion, particles suspended in pure water frequently collide with one another without coming into actual contact, but if an electrolyte is present the particles agglutinate, the Brownian motion ceases, and the flocks formed are deposited. The flocculation of liquids is not brought about by electrical action at a distance, as by Röntgen rays or the electricity developed by a statical machine or an induction coil, and cannot therefore be compared with the precipitation of dust particles in air. The feeblest electric current is, however, sufficient to induce clarification, which in the majority of cases commences at the cathode. Electrolytes of the same conductivity but having different anions and cations influence the flocculation very unequally. Electrolytes having the same cation induce flocculation in equal times, whilst the nature of the anion plays only a secondary part. The rate of flocculation in different electrolytes having the same anion is exactly in the order of the velocities of the cations in electrolysis. It therefore appears that the primary cause of the flocculation brought about by electrolytes is to be sought in the velocities of the ions. N. L.

Solid Solutions and Isomorphous Mixtures of Saturated and Non-saturated Open-chain Compounds. III. By GIUSEPPE BRUNI and F. GORNI (*Atti. Real Accad. Lincei*, 1900, [v], 9, ii, 151—156. Compare Abstr., 1899, ii, 731).—The isomorphism existing between stilbene and dibenzyl (*loc. cit.*) is also observed in their *pp*-dimethyl-derivatives. Stilbene, diphenylmethane, and diphenylamine do not form isomorphous mixtures as is the case with phenanthrene, fluorene, and carbazole, although the three compounds of each group are similarly related to one another. Neither cinnamic nor *allocinnamic* acid forms solid solutions with phenylacetic acid, but this property is exhibited by *p*-nitrobenzoic acid and *p*-nitrobenzaldehyde. T. H. P.

Limits of the Solid State. V. By GUSTAV TAMMANN (*Ann. Phys.*, 1900, [iv], 3, 161—194. Compare Abstr., 1899, ii, 635).—For pressures between 1 and 1200 kilograms per sq. cm. (the corresponding melting points being 5.4° and 36.5°), the latent heat of fusion of benzene has the mean value 30.7 cal., and does not vary appreciably. The volume changes accompanying fusion have been determined at different points on the melting point curve for benzene, naphthalene, phosphorus, and dimethylethylcarbinol; the volume change is found to diminish proportionally to the rising temperature of fusion, although considerable deviations from this rule are noted in the case of benzene above 60°. The volume change accompanying the transition of rhombic into monosymmetric sulphur is practically the same for all points on the transition point curve. The lowering of the freezing

point due to foreign substances increases markedly with rising pressure.

The author then discusses the general form of the melting point curve in the light of these results. His previous contention that the volume change and latent heat of fusion do not simultaneously become zero is upheld. Further, in the case of a transition, when the volumes of the two phases are equal, one at least being crystalline, the transition is accompanied by a change of energy. J. C. P.

Equilibrium between Lead and Zinc, and Mixtures of their Fused Chlorides. By W. REINDERS (*Zeit. anorg. Chem.*, 1900, 25, 126—145).—When a mixture of fused zinc and lead chlorides is electrolysed between carbon poles with a potential difference of 15—30 volts, the metallic regulus formed consists almost entirely of lead, even when the percentage of lead chloride in the fused mixture is small. At the temperature of the experiments (515°) zinc and lead are only partially miscible, and it might be expected that the curve connecting the percentage of lead in the regulus with the percentage of lead chloride in the fused mass would show a discontinuity. The curve, however, is found to be continuous, and it is suggested that in the electrolysis the proportions of the two metals liberated are not those which are in equilibrium with the fused mixture. A simple assumption would be that they are separated in the same ratio in which they are present in the fused mixture, and that the establishment of equilibrium is a subsequent and secondary process. Experiments were made in which zinc, zinc chloride, and lead chloride were shaken up together for several hours at 515°. The greater portion of the lead is found in the regulus at the end of the experiment, and it appears that in all cases where the percentage of lead chloride in the fused mixture is greater than 0.1, the regulus consists almost exclusively of lead.

If lead and zinc were miscible in all proportions the potential difference regulus | fused mixture would change continuously from the value for Pb | PbCl₂ to that for Zn | ZnCl₂. Since, however, the metals are only partially miscible, this will not be the case. When a mixture of the fused salts is in equilibrium, (1) with the saturated solution of zinc in lead, (2) with the saturated solution of lead in zinc, the potential differences in the two cases should be equal. This is borne out by experiment, for it is found that the E.M.F. of the combination 89.36Pb 10.64Zn | 99.9ZnCl₂ 0.1PbCl₂ | PbCl₂ | Pb is the same as that of the combination 3.16Pb 96.83Zn | 99.9ZnCl₂ 0.1PbCl₂ | PbCl₂ | Pb, namely, 0.278 volt at 515°. The potential difference Pb | PbCl₂ is raised by the addition of zinc. J. C. P.

Solubility of Carbonates of Alkaline Earths in Water containing Carbon Dioxide. By GUIDO BODLÄNDER (*Zeit. physikal. Chem.*, 1900, 35, 23—32).—The formulæ representing the equilibrium between carbonates, bicarbonates, and carbon dioxide are deduced, these leading to the result $K \cdot \text{CO}_2 = k(\text{HCO}_3)_3$, or $\text{HCO}_3/k \sqrt{\text{CO}_2} = \sqrt[3]{k}$. The values for $\sqrt[3]{k}$ are hence determined for solutions of calcium and barium carbonates, with results satisfactorily constant. The case of

magnesium carbonate is more complicated on account of the solubility of the hydrated magnesium carbonate, but this being taken into consideration, concordant results are obtained. The hydrolysis is also calculated for each of the compounds, and it is shown that the bicarbonates can only exist in solution in the presence of free carbon dioxide.

L. M. J.

Theory of the Fractional Precipitation of Neutral Salts and its Application in Analytical Chemistry. By ALEXANDER FINDLAY (*Zeit. physikal. Chem.*, 1900, 34, 409—436).—The author has studied the reversible reaction $\text{PbSO}_4 + 2\text{NaI} \rightleftharpoons \text{PbI}_2 + \text{Na}_2\text{SO}_4$, and found that the equilibrium constant given by the equation $K = C_i^2/C_s$, where C_i and C_s are the concentrations of the iodine and sulphate ions respectively, has a value between 0.25 and 0.30 at 25°. This result was obtained analytically, lead sulphate and iodide being shaken up with a mixed solution of sodium sulphate and iodide until equilibrium was established. The degrees of dissociation of the salts in the mixed solution were calculated by Kay's method (this vol., ii, 198).

The equilibrium constant of such a reaction as this defines the extent to which a separation of two salts by fractional precipitation can be effected. The addition of a soluble lead salt to a mixed solution of sodium iodide and sulphate causes the precipitation of lead iodide when the ratio C_i^2/C_s in the solution is greater than K ; when, by the removal of iodine ions, the ratio C_i^2/C_s has become equal to K , further addition of soluble lead salt precipitates both sulphate and iodide. When the ratio C_i^2/C_s in the solution is less than K , lead sulphate is precipitated first. A few experiments showed that the rate of precipitation of lead iodide is greater than that of lead sulphate.

The values of K obtained analytically were confirmed electrically. The E.M.F.s of the electrodes $\text{Pb} \mid \text{PbI}_2, \text{NaI}$ and $\text{Pb} \mid \text{PbSO}_4, \text{Na}_2\text{SO}_4$ were determined separately with the help of a normal electrode, and combination of the values for the separate electrodes gave the E.M.F. II of the cell $\text{Pb} \mid \text{PbI}_2, \text{NaI} \mid \text{Na}_2\text{SO}_4, \text{PbSO}_4 \mid \text{Pb}$. From theoretical considerations $\text{II} = 0.02953 \log.(K/a)$, where K is the equilibrium constant and a the ratio C_i^2/C_s in the solutions employed. The values of K calculated from this equation agree with those obtained analytically.

J. C. P.

Studies on Inversion. I. By ERNST COHEN (*Proc. K. Akad. Wetensch. Amsterdam*, 1900, 2, 618—634).—Rayman and Šulc (Abstr., 1897, ii, 136) have shown that solutions of cane sugar in very pure water undergo inversion with a steadily increasing velocity, and Kullgren finds, further, that non-electrolytes, such as glycerose and sucrose, exert a retarding influence on the hydrolysis of ethyl acetate by sodium hydroxide, due probably to the formation of a sodium derivative of the sugar. The author has extended these investigations on the apparent acidic nature of the sugars, by studying the effect of sucrose, invert sugar, dextrose, lævulose, and mannitol on the velocity of hydrolysis of $N/40$ ethyl acetate by $N/40$ sodium hydroxide at 25°.

The following table gives the velocity constants for various concentrations of the different sugars, the value for pure water being 6.86 :

	Concentration of Sugar.				
	N/5.	N/10.	N/20.	N/40.	N/80.
Sucrose	2.01	3.12	4.29	5.19	5.88
Invert sugar	0.38	0.67	1.17	2.03	3.38
Dextrose.....	0.79	1.37	2.32	3.69	4.79
d-Lævulose	0.59	1.02	1.88	3.04	4.27
Mannitol.....	5.17	5.85	6.18	6.40	6.81

Thus, whilst mannitol resembles methyl and ethyl alcohols (Kullgren) in exerting but a slight influence on the velocity of hydrolysis, the sugars, on the other hand, have a considerable retarding effect.

T. H. P.

Action of Bromine on Phenylsulphonacetic Acid and α -Phenylsulphonpropionic Acid in Aqueous Solution : a Contribution to Chemical Kinetics. By LUDWIG RAMBERG (*Zeit. physikal. Chem.*, 1900, **34**, 561—592).—Bromine reacts with phenylsulphonacetic acid in several stages ; the first two of these, consisting in the formation of mono- and di-bromophenylsulphonacetic acids, takes place with velocities which are approximately in the ratio 1.6 : 1. When the concentration of the bromine is high and the halogen is in excess, the reaction velocity is nearly proportional to the product of the concentration of the reacting acid and the square root of the bromine concentration. When the bromine concentration is low, the reaction velocity is proportional to the product of the concentrations of the reacting substances ; the lower the concentration, the more accurately does this rule apply. In explanation of the somewhat complicated phenomena, the author supposes that the bromine molecules in the solution are split into atoms to an extent depending on the concentration, and that only these atoms take part in the reaction.

The reaction between bromine and α -phenylsulphonpropionic acid, which is a case of simple substitution, has also been studied. The reaction velocity is found to depend in the same manner as above on the concentrations of the reacting substances. The relative velocity of the reactions becomes greater with increasing dilution.

The paper contains also a short account of the action of iodine on phenylsulphonacetic acid, and the formation therefrom of phenyldiiodomethylsulphone. The reaction does not lend itself to investigation on the lines indicated above.

J. C. P.

Physical Condition of Substances Insoluble in Water formed in Gelatin. By CORNELIS A. LOBRY DE BRUYN (*Rec. Trav. Chim.*, 1900, **19**, 236—249).—Details of work already published (this vol., ii, 136).

N. L.

G. Linck's Crystallographic Views. By GOTTLÖB LINCK (*Ber.*, 1900, **33**, 2284—2287).—The author replies to the criticisms of Muthmann (this vol., ii, 533) by quoting a number of observations to prove the validity of his crystallographic method for correcting atomic weights.

E. G.

Laboratory Apparatus. By FREDERICK W. STREATFEILD and FRANK SOUTHERDEN (*Chem. News*, 1900, 82, 56).—To aid in the distillation of substances which tend to solidify in the condenser, a second tube is passed through the inner tube; into this steam can be admitted when any obstruction is threatened.

A second apparatus is to serve for drying substances in a current of hot air previous to taking the melting points. The substance is placed on a piece of drying paper in the horizontal limb of a piece of bent combustion tube held in a clamp, the other limb is turned downwards at an angle of 140° and is heated by a Bunsen burner. The temperature can be adjusted by manipulating the flame, and is recorded and controlled by a thermometer suspended horizontally with the bulb just above the substance.

D. A. L.

Modification of the Water Vacuum Pump. By MARTIN H. ITTNER (*Amer. Chem. J.*, 1900, 24, 253—255).—The author has devised an improved form of the water-pump, which has been found to be well adapted for distillation under low pressures. The most important point is that the water supply is drawn from a large bottle, the water level in which is kept constant, so that no water will be drawn back into the vessel which is being exhausted and the pressure is not liable to variation by bubbles of air being carried over into the pump with the water. For details, the diagram in the original must be consulted.

E. G.

Economical Constant Gas Generator. By GEORG AUGUST KOENIG (*Zeit. anal. Chem.*, 1900, 39, 508—511).—This generator is designed both to check the waste of hydrogen sulphide which occurs in many laboratories and to furnish the gas instantly even when the laboratory temperature is too low for dilute sulphuric acid to react with ferrous sulphide. The ferrous sulphide is contained in a tubular vessel with a water jacket which is kept at 80° by a small flame. The acid drops in at the top of the generator from a stopcock thistle funnel. This funnel can be replenished from a reservoir, but if made to hold 50 c.c. and supplied with $N/2$ acid, a single filling suffices for almost any qualitative reaction. The neutralised acid flows away by a wide-bore stopcock and rubber tube at the lower end of the generator; only about 5—8 per cent. of the acid escapes neutralisation.

M. J. S.

Inorganic Chemistry.

Influence of Finely Divided Platinum on the Combination of Hydrogen and Oxygen. By WILLIAM FRENCH (*Chem. News*, 1900, 81, 292—294. Compare *Proc.*, 1897, 13, 52).—Experiments are described in which oxygen and hydrogen in electrolytic mixture and thoroughly dried did not combine when exposed to dry platinum sponge, although the same mixture exploded when ignited or when

brought into contact with moist platinum sponge especially in presence of light. D. A. L.

Action of Permanganate on Hydrogen Peroxide and on Caro's Acid. By ADOLF VON BAEYER and VICTOR VILLIGER (*Ber.*, 1900, 33 2488—2497).—Berthelot, who noticed that, when a dilute sulphuric acid solution of potassium permanganate is added to hydrogen peroxide at -12° , the colour of the mixture disappears without the evolution of oxygen, attributed this result to the formation of the peroxide H_2O_3 (*Abstr.*, 1880, 444). This explanation, however, is incorrect, the phenomenon being one of supersaturation; the gas is readily evolved on shaking the solution and the rate of evolution depends on the temperature; the time required for the liberation of the theoretical amount at -16° is 20 minutes, whilst at $+15^{\circ}$ this velocity is doubled.

A given quantity of potassium permanganate evolves more oxygen when mixed with Caro's acid than with hydrogen peroxide. Bach supposed that this was due to the existence of a higher peroxide H_2O_4 (this vol., ii, 470). This view of the reaction is erroneous, the result being due to a catalytic decomposition of Caro's acid. The amounts of oxygen evolved vary with the temperature and at 0° , 18° , and 34° they are equal, respectively, to 2.5, 3.5, and 4.5 times the volume of the gas evolved from hydrogen peroxide. The Caro's acid employed by Bach consisted of a mixture of this reagent with hydrogen peroxide, the latter substance first reduces a portion of the permanganate to manganous sulphate, a portion of the Caro's acid then oxidises this salt to manganic sulphate, the peroxidised salt subsequently acting catalytically on the remainder of the oxidising agent decomposing it with the evolution of oxygen. This catalytic decomposition of Caro's reagent depends on the presence of manganous sulphate, an acid solution of potassium permanganate having no immediate action on pure Caro's acid; excess of the proto-salt, however, exercises a retarding influence, and when it is added to the reacting mixture at the commencement of the experiment, the time required to complete the decomposition is 3 hours instead of 20 minutes.

The paper contains a discussion of the explanations put forward by Schönbein, by Weltzien and Traube, and by Berthelot to account for the reaction between hydrogen peroxide and permanganic acid.

Pure Caro's acid is prepared by triturating potassium persulphate with concentrated sulphuric acid and pouring the mixture on to chopped ice; the solution thus produced is shown to be free from hydrogen peroxide by testing with titanousulphuric acid. A dilute sulphuric acid solution of Caro's acid and potassium permanganate may be employed in testing the relative stability of organic compounds towards oxidising agents. The liquid paraffins ("Benzin") decolorise the solution very slowly, hexamethylene more rapidly, and benzene immediately.

Oxalic and succinic acids are exceedingly stable towards this reagent whilst phthalic and adipic acids are rapidly attacked. G. T. M.

Autoxidation. By FRITZ HABER (*Zeit. physikal. Chem.*, 1900, **34**, 513—521).—A discussion of the theory of oxidation both in absence and in presence of water. The equation $O_2 + 2H_2O \rightleftharpoons 2H_2O_2$ is resolved into the two others: (1) $O_2 \rightleftharpoons O + O$, (2) $O_2 + H_2O \rightleftharpoons H_2O_2 + O$. These two equations indicate the connecting link between the phenomena of oxidation in presence of water and those in absence of water. The slowness of many reactions in absence of water is then to be accounted for by the different reaction velocities of the equations (1) and (2). The author treats the subject also from the purely dynamical point of view.

J. C. P.

Autoxidation. II. By FRITZ HABER and FR. BRAN (*Zeit. physikal. Chem.*, 1900, **35**, 81—93).—Ostwald has attributed autoxidation to the formation of intermediate peroxides, and has shown that the two processes must be capable of expression by definitely connected equations. The author shows that this is the case if autoxidation in the presence of water is attributed to the formation of hydrogen peroxide, and in all the cases examined (namely, the following pairs, sodium sulphite and sodium arsenite, sodium sulphite and nickelous hydroxide, indigo and benzaldehyde, triethylphosphine and indigo, potassium ferrocyanide and benzaldehyde), one of the compounds is reactive with hydrogen peroxide, whilst the other is not. The equations representing the oxidation may be written $M + O_2 + H_2O = MO + H_2O_2$; $M + H_2O_2 = M(OH)_2$ (compare this vol., ii, 593, and preceding abstract).

L. M. J.

Change in Composition of Liquid Air on Evaporation. By A. A. GROUSINOFF (*J. Russ. Phys. Chem. Soc.*, 1900, **32**, ii, 107—114).—Liquid air, obtained from Linde's apparatus, was allowed to evaporate from a Dewar vacuum tube, the gas formed being collected and analysed. The results show that the law expressing the change in composition of liquid air on evaporation is independent of the speed of evaporation. From the numbers obtained, curves are constructed showing the variation of the percentage of oxygen with the proportion of the air evaporated, and also the percentage of oxygen at any time during the evaporation. These curves show that the liquid air prepared by Linde's apparatus contains 32.5 per cent. of oxygen which is reduced to the normal proportion (21 per cent.) after 40 per cent. of the liquid has evaporated.

T. H. P.

Nature of the Accessory Combustible Gases in the Air of Paris. By ARMAND GAUTIER (*Compt. rend.*, 1900, **131**, 535—539).—The ratio of carbon to hydrogen in the products of combustion of the air of Paris, after the hydrogen present in the free state (this vol., ii, 537, 538) has been taken into account, is always higher than that corresponding with methane. The reaction with iodic anhydride shows that this highly carburetted gas is not an olefine or an acetylene, and it is therefore in all probability benzene and its analogues, or some of the pyrogenic hydrocarbons. Assuming it to be benzene, the combustible constituents in 100 litres of Paris air are,

on an average, hydrogen, 19.5 c.c. ; methane, 12.1 c.c. ; benzene and its analogues, 1.7 c.c. ; carbon monoxide with traces of olefines and acetylenes, 0.2 c.c.

C. H. B.

Formation of Ozone by a Point-discharge in Oxygen. By EMIL WARBURG (*Sitzungsber. k. Preuss. Akad. Wiss.*, 1900, 712—721).—A formula is deduced for the rate of formation and decomposition of ozone by means of a point-discharge in oxygen, and has been verified by experiments carried out in a 'differential ozonometer' in which the amount of ozone produced is determined from the decrease or increase of pressure. The maximum percentage of ozone by volume was found to be 5.74 at -71° , 4.19 at 0° , 3.53 at 17° , 2.22 at 50° , and 1.23 at 93° , and the rates at which the ozone is produced and decomposed at each of these temperatures were determined separately by measuring the velocity of change. In a second series of experiments, a negative point-discharge was found to give about three times as much ozone as a positive discharge at 0° , 19° , and 48° . T. M. L.

Ozone. IV. By ALBERT LADENBURG (*Ber.*, 1900, 33, 2282—2284).—A reply to Brunck (this vol., ii, 572), who has recently cast doubt on the validity of the author's determinations of the molecular weight of ozone.

E. G.

Molecular Weight and Vapour Density of Sulphur. By OTTO BLEIER and LEOPOLD KOHN (*Monatsh.*, 1900, 21, 575—620).—As the numbers previously obtained (this vol., ii, 203) do not exclude the possibility that the sulphur molecule is greater than S_8 , and that at the temperatures employed, partial dissociation had occurred, further series of determinations have been made. They show that at the same temperature but with slight increments in pressure the density of sulphur vapour gradually approaches the value eight, but so gradually that it never actually reaches it. As this has been proved for several temperatures it is concluded that the molecule of sulphur must contain eight atoms. The authors claim that their method for vapour density determinations of dissociated vapours under reduced pressure is free from the serious objections which have been raised against the V. Meyer method.

The sulphur obtained in the apparatus at the end of the experiments is the modification insoluble in carbon disulphide, but at the higher temperatures, namely, in diphenylamine vapour and occasionally in amyl benzoate vapour under reduced pressure and in an atmosphere of nitrogen, a black modification of sulphur with a high metallic lustre has been observed. This variety is only slowly volatile, burns with a bright luminous flame, and is less brittle than yellow sulphur. It is possible that it is identical with the substance known as Magnus's black sulphur or with the modification of sulphur described by Dietzenbacher (*Compt. rend.*, 1863, 56, 39), and there is a further possibility that it may contain organic matter.

After determinations in amyl benzoate vapour, part of the sulphur is often left as clear, oily drops, which solidify when touched.

J. J. S.

Action of Alkaline Hydroxides, of Water and of Hydrogen Peroxide on Nitrogen Iodide. By F. D. CHATTAWAY and K. J. P. ORTON (*Amer. Chem. J.*, 1900, 24, 318—330. Compare *Proc.*, 1899, 15, 18).

Action of Acids on Nitrogen Iodide. By F. D. CHATTAWAY and H. P. STEVENS (*Amer. Chem. J.*, 1900, 24, 331—341. Compare *Proc.*, 1899, 15, 19).

Formation and Constitution of Nitrogen Iodide. By F. D. CHATTAWAY and K. J. P. ORTON (*Amer. Chem. J.*, 1900, 24, 342—355. Compare *Proc.*, 1899, 15, 20).

Condition of Nitrous Acid in Aqueous Solutions. By A. V. SAPOSCHNIKOFF (*J. Russ. Phys. Chem. Soc.*, 1900, 32, 375—381).—At 0°, aqueous solutions of nitrous acid are stable but on heating, gradual decomposition takes place according to the equation: $3\text{HNO}_2 = \text{HNO}_3 + 2\text{NO} + \text{H}_2\text{O}$. The author has investigated the rate of this decomposition and also the conditions of equilibrium of aqueous nitrous acid in an atmosphere of nitric oxide, but no equilibrium constant could be determined. On mixing chloroform with an aqueous solution of nitrogen trioxide, the latter becomes distributed between the two solvents but the concentration ratio has not a constant value. T. H. P.

Reaction of Nitroso-derivatives. By ANGELO ANGELI and FRANCESCO ANGELICO (*Atti Real. Accad. Lincei*, 1900, [v], 9, ii, 44—46. Compare this vol., ii, 594).—The ready resolution of nitrohydroxylaminic acid into nitrous and hyponitrous acids which is brought about by the action of aldehydes or of metallic sulphites, is further exemplified by the action of nitroso-derivatives in which the nitrogen atom is tervalent in function. Thus nitrosobenzene is readily dissolved by an aqueous solution of sodium nitrohydroxylamine, yielding the sodium salts of nitrous acid and of nitrosophenylhydroxylamine. T. H. P.

Reduction of Nitrates by Lactic Acid. By LUDWIG VANINO and O. HAUSER (*Zeit. anal. Chem.*, 1900, 39, 506—507).—The dry nitrates of bismuth, mercury (both mercurous and mercuric), cadmium, silver, lead, cobalt, and nickel, are decomposed, with separation of the respective metals, when heated with lactic acid. The chlorides and sulphates of the same metals show no reduction, neither do the nitrates of aluminium, the alkaline earths, and alkalis. Ferric nitrate gives a black magnetic powder, but whether this is metallic iron has not been ascertained. M. J. S.

Preparation of Phosphorus Free from Arsenic. By EMILIO NOELTING and W. FEUERSTEIN (*Ber.*, 1900, 33, 2684—2685).—By distilling ordinary phosphorus twice with steam in a current of carbon dioxide, a product is obtained, which, on conversion into the red modification, and treatment with ammonium nitrate, yields no trace of arsenic; Winkler's view (this vol., ii, 476) as to Fittica's supposed transformation of phosphorus into arsenic is thus confirmed. W. A. D.

Composition of Soot from Mineral Coal. By H. WARTH (*Chem. News*, 1900, 82, 6).—The aqueous extract of the soot on evaporation gave a very hygroscopic mass; the ammonium salts were sublimed from it, and the residue was lixiviated with water to ascertain the proportion of fixed salts. The numbers obtained were: ammonium sulphate, 0.1; ammonium chloride, 7.3; non-volatile soluble salts, 1.3 per cent. of the original soot. D. A. L.

Krypton. By ALBERT LADENBURG and C. KRÜGEL (*Sitzungsber. K. Preuss. Akad. Wiss.*, 1900, 727—728. Compare this vol., ii, 540).—No simpler method of preparing krypton has yet been found than that already described (*loc. cit.*), and the 32 c.c., or 0.083 gram, isolated from 850 litres of liquid air probably represents the normal proportion of the gas in the atmosphere, which would thus be about 0.00001 per cent. The semi-solid residue from 3 litres of liquid air, when freed from carbon dioxide, nitrogen, and oxygen, gave a residue of argon but no krypton.

The density of the gas when purified by a further fractionation gave the value 59.01 for the molecular weight ($O_2 = 32$), confirming the earlier values and the hypothesis as to the position of krypton in the periodic system. T. M. L.

Action of Chlorine on Metallic Silver in the Light and in the Dark. By V. VON CORDIER (*Monatsh.*, 1900, 21, 655—670. Compare this vol., ii, 343).—Red light does not facilitate the union of chlorine and silver, but blue and violet light favour the combination, although in the latter cases reduction is also accelerated.

Light which has traversed a sufficiently thick layer of chlorine behaves very similarly to red light; the result depends largely on whether the chlorine used for filtering the light is dry or moist; if dry, the action is pretty much the same as when white light is used, but if the light is passed through moist chlorine a considerable diminution in the activity of combination is noticeable. The difference is even greater if a little hydrogen is added to the moist chlorine. Röntgen rays have no perceptible influence on the combination of chlorine and silver. J. J. S.

Some Complex Silver Salts. By KARL HELLWIG (*Zeit. anorg. Chem.*, 1900, 25, 157—188).—Silver iodide and nitrate exist in common solution as a complex salt; this is shown by the lowering of the boiling point due to the addition of the iodide to a solution of the nitrate. The solubility of the iodide in solutions of the nitrate has been determined, and the values obtained have been used in applying the law of mass action to the dissociation of the double salt; in this, experiment agrees fairly well with theory, although the presence of other complex salts than $Ag_3I(NO_3)_2$ seems to introduce a disturbing factor. When this double salt is electrolysed, the silver iodide is found to migrate to the cathode—a case of a complex cation. The solubilities, at 25° in 3*N* silver nitrate solution, of silver iodide,

bromide, chloride, cyanide, and thiocyanate are respectively 9.4, 2.13, 5.6, 9.1, 2.6 millimolecules per litre.

The tendency of insoluble silver salts to form complex anions has also been investigated. The solubility of these salts in the corresponding alkali salts is greatest for the cyanide, followed by the thiocyanate, iodide, bromide, and chloride. The author's observations are in good agreement with Abegg and Bodländer's theory (Abstr., 1899, ii, 542) regarding the formation of complex ions.

The existence of the following double salts in solid form has been confirmed: $\text{Ag}_3\text{I}(\text{NO}_3)_2$, Ag_2INO_3 , Ag_2BrNO_3 , $\text{Ag}_3\text{CN}(\text{NO}_3)_2$, K_2AgI_3 , KAgI_2 , $\text{KAg}(\text{CNS})_2$. The double salt, $\text{Ag}_3\text{CNS}(\text{NO}_3)_2$, has been prepared for the first time. J. C. P.

Silver Peroxysulphate and Peroxyacetate. By EDUARD MULDER (*Rec. Trav. Chim.*, 1900, 19, 115—165. Compare Abstr., 1896, ii, 561; 1897, ii, 260 and 551; 1899, ii, 483).—The first part of this paper is devoted to a detailed consideration of the preparation and properties of silver peroxysulphate, of which a short account has already been given (Abstr., 1899, ii, 483). The influence of experimental conditions on the yield and purity of the compound is discussed, and the factors of prime importance are shown to be the strength of the current, the concentration of the solution, the rate at which the solution is neutralised during the electrolysis, and the time. Details are then given of the analysis and products of decomposition of a number of different preparations, and some modifications and improvements in the various processes are described. The use of two filters is found advisable, the first containing silver carbonate to neutralise the free acid formed during electrolysis, whilst the second contains silver sulphate, whereby the concentration of the solution is maintained. The formation and decomposition of silver peroxysulphate are theoretically discussed, an analogy is drawn between oxysulphuric and persulphuric acids, and a structural formula for the former is suggested. Remarks are also made on the action of persulphuric acid on hydrogen peroxide, the behaviour of silver peroxide, peroxysulphate, and peroxynitrate as oxidising agents, the separation of oxynitric and oxysulphuric acids by dialysis, the rate of spontaneous decomposition of silver peroxysulphate and peroxynitrate, experiments on the yield of the latter salt as a function of the time, and the separation of silver nitrate and sulphate by means of alcohol. The general question of the formation of compounds of silver salts of oxyacids with silver peroxide is considered.

In the second part of the paper, an account is given of a preliminary series of experiments on the electrolysis of silver acetate. The most favourable conditions for the formation of the product at the anode are difficult to determine, and the analyses thereof are as yet incomplete, but the production of a compound of the general composition $x\text{Ag}_2\text{O}_{2,y}(\text{AgOAc},z\text{O})$, analogous to the peroxysulphate and peroxynitrate, is regarded as demonstrated. In the preparation of this substance, silver oxide is found to be better adapted than the carbonate for the neutralisation of the free acid formed. It is suggested that the further investigation of silver peroxyacetate will throw light on

the phenomena of the electrolysis of the salts of organic acids in general. N. L.

Solubility of Calcium Carbonate in Sea-water. By ERNST COHEN and H. RAKEN (*Proc. K. Akad. Wetensch. Amsterdam*, 1900, 3, 63—66).—Artificial sea-water, free from calcium carbonate, was agitated with this substance by means of a current of air, and excess of carbon dioxide subsequently expelled by a current of air free from this gas. In eight days, calcium carbonate corresponding with 53.94 milligrams, and in seventeen days with 57.27 milligrams of combined carbon dioxide per litre, was dissolved at 15°. Sea-water, which contains 52.8—55 milligrams of neutral combined carbon dioxide per litre, must therefore be saturated with calcium carbonate. G. T. M.

Orthoplumbates of the Alkaline Earths. IV. Lead "Peroxide." By GEORG KASSNER (*Arch. Pharm.*, 1900, 238, 449—458. Compare Abstr., 1899, ii, 657).—Calcium perplumbate, already obtained from the metaplumbate, can also be obtained from the crystallised orthoplumbate, $\text{Ca}_2\text{PbO}_4 \cdot 4\text{H}_2\text{O}$, by heating it, best in a current of oxygen, but also in a current of nitrogen or in a vacuum; its formation is due to an intramolecular transformation or oxidation. The temperature employed should be about 260—280°, and the heating should not be continued too long (about 2 hours suffice). C. F. B.

Some Isomeric Halogen Compounds of Thallium and the Constitution of Double Salts. By ALLERTON S. CUSHMAN (*Amer. Chem. J.*, 1900, 24, 222—242).—When thallous chloride is shaken with bromine and water, and afterwards dissolved in boiling water acidified with nitric acid, the compound, $\text{TlClBr}_2 \cdot 3\text{TlCl}$, separates on cooling in orange-coloured, hexagonal plates.

If thallous bromide is suspended in hot water and treated with solution of thallic chloride, the compound, $\text{TlCl}_3 \cdot 3\text{TlBr}$, is deposited in orange, hexagonal plates; under similar conditions, thallous chloride unites with thallic bromide to form an isomeric compound, $\text{TlBr}_3 \cdot 3\text{TlCl}$, which dissolves on boiling, and, if the solution is rapidly cooled, is obtained in blood-red, hexagonal crystals. The former compound is very stable, and can be crystallised from water unchanged; its red isomeride, on the other hand, is very unstable and easily decomposed by water. If the orange compound, $\text{TlCl}_3 \cdot 3\text{TlBr}$, is treated with excess of thallic chloride, the sesquichloride, $\text{TlCl}_3 \cdot 3\text{TlCl}$, is produced, whilst by the action of thallic bromide, long, yellow needles of the double salt, $\text{TlBr}_3 \cdot \text{TlCl}$, are obtained, which on recrystallisation from water are converted into dark red crystals of $\text{TlBr}_3 \cdot 3\text{TlCl}$. In the process of preparing the red compound by the action of thallous chloride on thallic bromide, it was found possible, by varying the dilution, to obtain directly the yellow needles, $\text{TlBr}_3 \cdot \text{TlCl}$, the orange compound, $\text{TlCl}_3 \cdot 3\text{TlBr}$, or the red compound, $\text{TlBr}_3 \cdot 3\text{TlCl}$.

In order to elucidate the constitution of these double salts, determinations were made of the electrical conductivity of solutions of the thallium chlorides and bromides; the results "appear to find a more rational explanation under Werner's hypothesis than under the old linkage theory." E. G.

Preparation and Properties of Neodymium and Praseodymium Carbides. By HENRI MOISSAN (*Compt. rend.*, 1900, 131, 595—600. Compare Abstr., 1896, ii, 422).—*Neodymium carbide*, NeC_2 , prepared by gently calcining a compressed cylindrical mass of neodymium oxide, Ne_2O_3 , and sugar carbon moistened with turpentine until combustible gases are no longer evolved, and then heating the residue for four minutes in the electric furnace by means of a current of 900 amperes and 50 volts, is obtained in the form of yellow, hexagonal plates of sp. gr. 5.15.

Praseodymium carbide, PrC_2 , produced in similar manner by substituting praseodymium oxide, PrO_2 , for the neodymium compound in the above experiment, closely resembles the preceding carbide; it has a sp. gr. 5.10.

These substances are not reduced by hydrogen at a red heat. Nitrogen or ammonia attacks the carbides at 1200° , the former gas forming nitrides and the latter a mixture of hydrides and nitrides; the product in the second case evolves hydrocarbons and ammonia on treatment with water.

When the carbides are greatly warmed in fluorine, a vigorous action takes place accompanied by incandescence; the resulting fluorides are insoluble in water, and somewhat infusible and non-volatile. The halogens act on the carbides only at red heat, the intensity of the action diminishing from chlorine to iodine; the anhydrous haloid salts produced are all soluble in water. A soluble product is likewise obtained by the action of hydrogen chloride at a dull red heat. When heated at 400° in a current of oxygen, neodymium carbide is completely decomposed, leaving a mauve oxide; praseodymium carbide, when similarly treated, yielding a black oxide. Sulphur and hydrogen sulphide, at temperatures between 400° and 1000° give rise to sulphides which are decomposed by water or dilute acids. Carbon readily dissolves in the fused carbides, and the cooled product presents a fracture similar to that of plumbago owing to the presence of graphite crystals.

Water decomposes these carbides as readily as those of cerium, lanthanum, and yttrium, a mixture of gaseous hydrocarbons being evolved, whilst the residue consists of liquid and solid hydrocarbons and hydrated oxides. The composition of the gaseous mixture is very similar in both cases, the gas consisting of acetylene (65 to 68 per cent), olefines (2.5 to 7 per cent.), and paraffins (27 to 30 per cent.). Hot concentrated sulphuric acid is reduced by the carbides yielding sulphur dioxide. Dilute nitric acid rapidly oxidises these compounds, yielding the metallic nitrates; the concentrated acid has no action on them.

The carbides of the cerium group of metals evolve a mixture of hydrocarbons, and differ markedly from those of alkaline-earth series which yield acetylene only, and also from aluminium carbide, which furnishes methane.

G. T. M.

Hydroxides of Aluminium. By EUGENE T. ALLEN (*Chem. News*, 1900, 82, 75—76).—The author is of opinion that precipitated alumina has the composition $\text{Al}(\text{OH})_3$, whether prepared by pre-

precipitating warm or in the cold with ammonia, by boiling a soluble aluminate with ammonium chloride, by boiling the basic carbonate with water or dilute ammonia, or by the prolonged action of water on soluble aluminates. The last form is crystalline and does not lose water over sulphuric acid; the amorphous varieties under such conditions, or by heating at 100° , lose a mol. of water leaving the hydrate, $\text{Al}_2\text{O}_5\text{H}_4$, which is hygroscopic and reverts to $\text{Al}(\text{OH})_3$.

D. A. L.

Action of Caustic Hydroxides on Aluminium. By EUGENE T. ALLEN and H. F. ROGERS (*Amer. Chem. J.*, 1900, **24**, 304—318).—On dissolving aluminium in an excess of 10 per cent. aqueous potassium hydroxide, and evaporating the solution in a vacuum over sulphuric acid, the aluminate, $\text{K}_2\text{Al}_2\text{O}_4 \cdot 3\text{H}_2\text{O}$ (Freymy, *Ann. Chim. Phys.*, 1844, [iii], **12**, 362) separates in hard, nodular crystals; if the alkali is not in excess, hydrolysis of the aluminate occurs and crystalline aluminium hydroxide is deposited, whilst the metal continues to dissolve indefinitely instead of in the proportion demanded by Cavazzi's equation, $2\text{KOH} + 2\text{Al} + 2\text{H}_2\text{O} = \text{K}_2\text{Al}_2\text{O}_4 + 3\text{H}_2$ (Abstr., 1885, 1112).

A solution of aluminium in aqueous sodium hydroxide does not crystallise on evaporation, but on repeatedly digesting with alcohol a hard mass of *sodium aluminate*, $\text{Na}_2\text{Al}_2\text{O}_4 \cdot 4\text{H}_2\text{O}$, is obtained. *Lithium aluminate*, $\text{LiHAl}_2\text{O}_4 \cdot 5\text{H}_2\text{O}$, obtained in similar manner, is a light, micro-crystalline powder, sparingly soluble in water, by which it is decomposed only after continued boiling; one preparation contained 3 instead of $5\text{H}_2\text{O}$, but an aluminate of a different type could not be obtained.

Aluminium dissolves vigorously in hot concentrated aqueous barium hydroxide, yielding the aluminate $\text{Ba}_2\text{Al}_2\text{O}_5 \cdot 5\text{H}_2\text{O}$, as a heavy crystalline, moderately soluble powder, somewhat easily decomposed by water (compare Beckmann, Abstr., 1889, 289 and 649); in the cold, the compound, $\text{BaAl}_2\text{O}_4 \cdot 5\text{H}_2\text{O}$ (Beckmann gives $6-7\text{H}_2\text{O}$), is obtained, as a soft, white, apparently amorphous powder, which is easily decomposed by water and by carbon dioxide.

When aluminium is boiled with concentrated, aqueous strontium hydroxide, hydrogen is evolved for a moment, but no further action then occurs; in the cold, the metal dissolves and the *aluminate*, $\text{Sr}_3\text{Al}_2\text{O}_6 \cdot 6\text{H}_2\text{O}$, separates. The latter is better obtained by adding a solution of potassium aluminate containing an excess of potassium hydroxide to a hot solution of strontium chloride or hydroxide; it forms a white, heavy, granular, crystalline powder sparingly soluble in water, by which it is only slowly decomposed, and sensitive to the action of carbon dioxide. A second *aluminate*, $\text{SrAl}_2\text{O}_4 \cdot 4-5\text{H}_2\text{O}$, closely resembling the second barium aluminate may also be formed in the action of strontium oxide on aluminium, but could not be obtained pure; it forms a glutinous mass.

Calcium aluminate, $\text{Ca}_2\text{Al}_2\text{O}_5 \cdot 7\text{H}_2\text{O}$, obtained by dissolving aluminium in lime-water kept saturated with the hydroxide, is a dense, white, crystalline substance, with a pearly lustre; it is only slowly decomposed by water, in which it is very sparingly soluble. On adding aqueous potassium aluminate to hot lime-water, a crystalline

precipitate of the compound $\text{Ca}_3\text{Al}_2\text{O}_6 \cdot 6\text{H}_2\text{O}$ is obtained; it closely resembles the corresponding strontium compound. W. A. D.

Aluminates. By W. HERZ (*Zeit. anorg. Chem.*, 1900, 25, 155—156).—Alkali aluminates of the formula Na_3AlO_3 and K_3AlO_3 , are obtained in solution by shaking excess of aluminium hydroxide (prepared by precipitation with ammonia and dried in a vacuum desiccator) with solutions of alkali hydroxides of varying strength.

E. C. R.

Crystallised Monocalcium Aluminate. By ÉMILE DUFAU (*Compt. rend.* 1900, 131, 541—544).—When alumina which has been strongly ignited is heated in the electric furnace with 60 per cent. of its weight of calcium oxide, *calcium aluminate*, $\text{CaO} \cdot \text{Al}_2\text{O}_3$, is obtained in colourless, transparent needles softer than glass and of sp. gr. 3.671 at 20°. It is decomposed by water, but does not “set,” and is readily attacked by hydrochloric acid but not by nitric, sulphuric, or hydrofluoric acid. Fluorine attacks it only on heating, but chlorine, bromine, iodine, or sulphur has no action on it at the softening point of glass. When heated with carbon in the electric furnace, it yields two distinct carbides. Attempts to prepare polycalcium aluminates in the electric furnace gave negative results.

It is noteworthy that this calcium aluminate like the analogous beryllium compound, and like calcium chromate and calcium ferrite, does not belong to the group of the spinels. C. H. B.

Iron and Hydrogen. By E. HEYN (*Chem. Centr.*, 1900, ii, 621—622; from *Stahl. u. Eisen*, 20, 837—844).—When cast iron is heated at 730—1000° in contact with hydrogen and then chilled, it becomes considerably more brittle than when similarly heated in air and chilled. If, however, the metal is allowed to cool slowly in hydrogen, it remains tough, and at temperatures below 730° its properties are not affected by hydrogen. A cast iron containing 0.37 per cent. of carbon was found to behave in the same way as one containing only 0.05 of carbon and 0.01 of silicon. By heating the metal in nitrogen at a red heat, the effect of the treatment with hydrogen is destroyed, and in one experiment at a temperature of 820° hydrogen equal to 0.00019 per cent. of the weight of the iron was liberated. In the case of iron containing very little carbon, the brittleness is partly removed by heating in boiling water, or even by long exposure to the air at the ordinary temperature, and is completely destroyed by heating at 200—250°. Iron containing more carbon retains its properties much more obstinately. A superficial layer after treatment with hydrogen was found to show a greater flexibility, hence the hydrogen must penetrate below the surface. The density of the metal is not affected by the treatment with hydrogen. The change cannot be ascribed to silicon taken up from the porcelain tubes in which the metal was heated, for the same result is obtained when iron tubes are employed. E. W. W.

Iron and Steel from the Standpoint of the Phase Rule. By H. W. BAKHUIS ROOZEBOOM (*Zeit. physikal. Chem.*, 1900, 34, 437—487).—The author gives an exhaustive theoretical treatment of

the subject, comparing his conclusions, where possible, with the results obtained by Roberts-Austen and others. In developing the theory, much use is made of the facts recently established in connection with the formation and transformation of mixed crystals. The scheme deduced by the author as representing the equilibria in iron-carbon mixtures of varying composition and at different temperatures can be given only in outline.

Mixtures containing 0—2 per cent. of carbon solidify to homogeneous mixed crystals—martensite; mixtures with 2—4·3 per cent. of carbon solidify to a framework of these mixed crystals, surrounded by a eutectic product, consisting of mixed crystals and graphite; mixtures with more than 4·3 per cent. of carbon solidify to a framework of graphite crystals, surrounded by the eutectic product. On cooling below the solidifying temperature, the alloys with more than 2 per cent. of carbon undergo a separation of carbon between 1130° and 1000°, and at the latter temperature martensite and graphite are transformed into carbide or cementite (Fe_3C); so long as the carbon percentage is less than 6·6, this results in a conglomerate of martensite and cementite. The formation of the latter continues progressively down to 690°; during this interval, the martensite crystals become poorer in carbon, and contain ultimately no more than 0·85 per cent. They disappear at 690° and are transformed into α -iron (or ferrite) and cementite. Any deviations from this normal behaviour are to be regarded as due to unequal rate of cooling; it is certain that with rapid cooling cementite is formed at once, and that in the formation of cementite from the martensite and graphite, a portion of the latter always escapes transformation. Alloys with 2·0—0·85 per cent. carbon separate cementite between 1000° and 690°, resolving themselves at the latter temperature into cementite and ferrite. These changes may, however, fail to take place when the cooling is rapid, in which case the martensite crystals would be permanent. Alloys with 0—0·35 per cent. carbon gradually separate β -iron between 890° and 770°; at 770°, the β -iron is completely transformed into α -iron, and afterwards there takes place a gradual separation of α -iron from the mixed crystals remaining at 770°. Alloys with 0·35—0·85 per cent. carbon separate α -iron only between 770° and 690°. In all alloys with 0—0·85 per cent. carbon, a transformation of the remaining martensite crystals into ferrite and cementite takes place at 690°, although rapid cooling may prevent it. So far as published results go, it is possible to give another scheme of the changes taking place in alloys with 0—0·85 per cent. carbon, on the supposition that carbon is slightly soluble in β - and α -iron. In the author's scheme, a place is found for austenite, which is regarded as a mass of mixed crystals separating themselves from concentrated liquid solutions. Several points in the author's scheme tend to show that carbon is monatomic in solution, but the question is not definitely settled. The question of the diffusion of carbon in iron is also discussed.

J. C. P.

Iron Silicide, Fe_2Si , and its presence in Ferro-silicons. By PAUL LEBEAU (*Compt. rend.*, 1900, 131, 583—586).—Iron silicide,

Fe_2Si , is obtained by strongly heating iron with twice its weight of commercial copper silicide containing 10 per cent. of silicon, the product being treated with nitric acid (1:10) and purified in the usual way. It forms long, brilliant, grey crystals with octahedral terminations. In sp. gr. and chemical properties, it is identical with the silicide obtained by Moissan in the electric furnace (Abstr., 1896, ii, 173), and it can be isolated from commercial ferro-silicons which contain 10 to 20 per cent. of silicon and have been prepared at a high temperature. C. H. B.

Nickel Selenides. By HENRI FONZES-DIACON (*Compt. rend.*, 1900, 131, 556—558).—*Nickel selenide*, NiSe , is obtained in regular double tetrahedrons by the action of selenium vapour diluted with nitrogen on nickel at a dull red heat, and also by the action of hydrogen selenide on anhydrous nickel chloride at a bright red heat. *Nickel sesquiselenides*, Ni_2Se_3 and Ni_3Se_4 , are obtained by the action of hydrogen selenide on anhydrous nickel chloride at a dull red heat; the compound Ni_3Se_4 is grey and seems to crystallise in the cubic system. *Nickel diselenide*, NiSe_2 , is a dark grey compound formed when hydrogen selenide acts on anhydrous nickel chloride at about 300° . *Nickel subselenide*, Ni_2Se , is a golden-yellow compound obtained by the prolonged action of hydrogen on any of the preceding compounds at a bright red heat. An *oxyselenide* is found when the selenate is carefully heated in dry oxygen.

The selenides are but little affected by boiling hydrochloric acid, but are slowly decomposed by hydrogen chloride at a high temperature. They are readily decomposed by chlorine, and are oxidised by nitric acid with production of selenites, and also by oxygen when heated in that gas. C. H. B.

Periodic Phenomena in the Dissolution of Chromium in Acids. By WILHELM OSTWALD (*Zeit. physikal. Chem.*, 1900, 35, 33—76).—It has been shown by Hittorf that chromium is remarkable in its behaviour towards acids, assuming an active and a passive state in different circumstances (Abstr., 1898, ii, 363). The author, on investigating further the action of the active chromium on acids, observed a remarkable periodicity in the rate of evolution of the hydrogen, and constructed a self-registering apparatus in order to investigate this property. A piece of passive chromium rendered active by contact with cadmium under acid was dissolved in 2*N* hydrochloric acid; the curve obtained indicated an initial irregular action, which, after about 15 minutes, becomes periodic, the velocity rapidly increasing to a maximum and then falling more slowly to a minimum. The duration of each period was found to increase during the progress of the reaction. Various forms of curves are obtained from different pieces of chromium, and two pieces placed in the same acid were found to give a double summation curve, so the cause of the periodicity lies in the metal and not in the acid. The influence of acid concentration, of temperature, and of foreign substances was studied. Some compounds cause a lengthening of the period, formaldehyde has a remarkably great effect, whilst nitric acid and nitrogen oxides accelerate the periodicity, as also do chloric and bromic acids to a less marked

extent. A piece of almost pure chromium supplied to the author by Goldschmidt did not exhibit these periodic phenomena, neither could it be made active in this respect by treatment with any reagents.
L. M. J.

Constitution of Uranyl Salts. By HEINRICH LEY (*Ber.*, 1900, 33, 2658—2661).—The author has redetermined the conductivities of solutions of uranyl nitrate with specially purified materials, and the results confirm those previously obtained (this vol., ii, 67).

With uranyl nitrate $\mu 1024-\mu 32$ is 33.4 at 25° , whilst with barium nitrate the corresponding number is 23.1 , so that the hydrolytic dissociation of the former in aqueous solution at the dilution $1 : 1024$ does not exceed 5 per cent. Dittrich (*Abstr.*, 1899, ii, 629), found the hydrolytic dissociation of uranyl nitrate in 10 per cent. aqueous solution to be 3.6 per cent. at 65° , using the method of cane sugar inversion.

Uranyl salts of strong acids therefore, contrary to the view taken by Kohlschütter (this vol., ii, 484), who regarded the chloride as analogous to acyl chlorides, behave like the corresponding salts of aluminium and beryllium, and are for the most part normally ionised, the radicle UO_2 being the cation.
A. L.

Behaviour of some Halogen Compounds of the Carbon Group analogous to Stannic Chloride. By WL. VON KOWALEWSKY (*Zeit. anorg. Chem.*, 1900, 25, 189—195).—The method of investigation described in a previous paper (this vol., ii, 256), has been applied to titanium tetrachloride and tetrafluoride, and silicon tetrachloride. A solution of titanium tetrachloride in water forms a voluminous precipitate, which dissolves again at the ordinary temperature, without any corresponding change in conductivity. The value of the conductivity points to equilibrium being established before hydrolysis is complete; the hydrolysis is completed by boiling, or by heating in a sealed tube at 150° .

The results show that the tendency to hydrolysis of the tetrachlorides diminishes from tin to titanium and to silicon; the same remark applies to their ability to form complex salts.
J. C. P.

Alloys of Antimony and Tin. By W. REINDERS (*Zeit. anorg. Chem.*, 1900, 25, 113—125).—The freezing point curve for alloys of these two metals has been traced and interpreted; it consists of four branches, the three points of intersection occurring at 8, 20, and 51 per cent. of antimony, and at the temperatures 243° , 310° , and 430° . As found previously by Heycock and Neville (*Trans.*, 1890, 57, 387), the first branch of the curve, starting from pure tin, immediately rises, and there is no eutectic point below the melting point of tin.

These results have been supplemented by an investigation of the microscopic structure of the alloys, the polished sections being etched by electrolytic oxidation in dilute nitric acid. In alloys containing less than 8 per cent. of antimony, mixed crystals of tin and antimony are traced, of the same form as tin crystals. In alloys with 8—20 per cent., cubic crystals are first formed. The crystals characteristic of the third branch of the freezing point curve were somewhat undefined in

form; those of the fourth branch are of the antimony type. In some cases, the crystals first formed could be detected, even though theory required their disappearance under the existing conditions; this is probably due to those crystals getting coated in the rapid cooling, and so being protected from further interaction and transformation.

J. C. P.

Pentachloroplatinic Acid. By ARTURO MIOLATI and I. BELLUCCI (*Atti Real. Accad. Lincei*, 1900, [v], 9, ii, 51—57 and 97—102).—The compound $\text{PtCl}_4 \cdot \text{HCl} \cdot 2\text{H}_2\text{O}$, obtained by Pigeon (Abstr., 1891, 1325) by heating chloroplatinic acid in presence of fused potassium hydroxide, is found to be the intermediate term between chloroplatinic acid and tetrachloroplatinic acid, $[\text{PtCl}_4(\text{OH})_2]\text{H}_2$; it separates as a reddish-brown, deliquescent mass which gives a pale yellow, acid, aqueous solution readily decomposing carbonates in the cold. With ammonia solution, it gives no precipitate, and on heating the liquid it becomes almost colourless. Ammonium and potassium chlorides precipitate the respective platinichlorides. Comparison of the values of the electrical conductivity of solutions of various strengths of the acid with the corresponding numbers for oxalic and hydrofluosilicic acids show it to be dibasic, as also does titration with sodium hydroxide solution. Conductivity experiments also show that one of the replaceable hydrogen atoms of the molecule has a strongly acid character, the other having only weak acid properties. The *sodium* salt, $\text{OH} \cdot \text{PtCl}_5\text{Na}_2$, exists only in solution whilst the *lithium* salt separates in the form of small, yellow needles which are very hygroscopic; the *barium* salt, with $4\text{H}_2\text{O}$, forms long, orange-yellow prisms, and the *silver* salt a yellowish precipitate stable in boiling water; the *thallium* salt and basic *lead* salt, $\text{PtCl}_5(\text{OH})\text{Pb} \cdot \text{Pb}(\text{OH})_2$, were also prepared.

T. H. P.

Platinum Tetrabromide. By ARTURO MIOLATI and I. BELLUCCI (*Atti Real. Accad. Lincei*, 1900, [v] 9, ii, 140—146).—On mixing solutions of a metallic salt and platinum tetrabromide, salts are precipitated corresponding with tetrabromoplatinic acid, $\text{PtBr}_4(\text{OH})_2\text{H}_2$. The *silver* and *thallium* salts form tobacco-coloured precipitates, the basic *lead* salt, $\text{PtBr}_4(\text{OH})_2\text{Pb} \cdot \text{Pb}(\text{OH})_2$, a dark brown powder and the *mercury* salt a brown precipitate. The electrical conductivity of solutions of platinum bromide by itself and also when mixed with varying quantities of alkali, shows that tetrabromoplatinic acid is a dibasic acid, and that only one of the replaceable hydrogen atoms is strongly dissociated in solution. The acid dissolves lithium carbonate with evolution of carbon dioxide.

T. H. P.

Behaviour of Rhodium in Alloys with the Noble Metals. By HEINRICH RÖSSLER (*Chem. Zeit.*, 1900, 24, 733—735. Compare Mietzschke, this vol., ii, 371).—When rhodium is cupelled with lead and silver, the button is left with a grey coating of metallic rhodium, which, after removal of the silver, appears as microscopic, six-sided plates and ladder- or star-shaped crystal aggregates. If merely added to molten silver, it floats on the surface of the button and is recovered

in the amorphous state. Rhodium, therefore, does not alloy with silver, and further its density must be less than 12.1.

Rhodium alloys with molten gold, and gives evidence of real combination, an alloy containing 1 per cent. being entirely soluble in aqua regia. A 10 per cent. admixture yields the free metal as feather- or rowel-shaped crystal aggregates, whilst if this limit is exceeded, amorphous rhodium is also found when the button is dissolved in nitro-hydrochloric acid.

Rhodium (2—5 per cent.) added to molten bismuth forms the compound RhBi_4 , which remains after treatment with nitric acid as glistening needles appearing under the microscope as crystalline aggregates. From richer alloys the metal is recovered in a crystalline or amorphous condition, according to the proportion used. If the metals are fused together in the proportions represented by the above formula (12 : 88), the resulting mass is entirely soluble in aqua regia or strong boiling nitric acid, but dilute nitric acid does not dissolve out the bismuth separately.

Iridium behaves like rhodium with silver under the conditions described, but this metal sinks in the button and its crystals are eight-sided. When cupelled with lead and gold, or merely fused with gold, it remains amorphous and shows no solubility in aqua regia.

Small quantities of platinum, in gold ingots (a few parts per thousand) are estimated by boiling out one of two similar cornets with concentrated sulphuric acid ; the other with nitric acid. The excess in weight of the first over the second is reckoned as platinum. For larger quantities up to twenty parts per thousand, the second cornet is treated twice. For still larger quantities, the silver is first removed by sulphuric acid, the residue is dissolved in dilute aqua regia (avoiding excess of nitric acid), which leaves any rhodium and iridium behind, whilst the gold in the filtrate is precipitated with ferrous chloride. If ferrous sulphate is used, platinum may be precipitated with the gold.

R. L. J.

Mineralogical Chemistry.

Genesis of some Scottish Minerals. By JOHN GEORGE GOODCHILD (*Proc. R. Physical Soc. Edinb.*, 1900, 14, 181—220).—A speculative paper. L. J. S.

Cinnabar-bearing Trachyte-tuff from South Tuscany. By JOHAN H. KLOOS (*Zeit. Kryst. Min.*, 1900, 33, 206 ; from *Zeit. prakt. Geol.*, 1898, 158—163).—A decomposed trachyte from Monte Amiata was found to contain 2·76—5·36 per cent. of mercury. Felspar-sand contained 0·35—54·35, and a kaolin 4·80 per cent. of mercury as cinnabar. L. J. S.

Manganese Ore from the Amazon District. By FRIEDRICH KATZER (*Zeit. Kryst. Min.*, 1900, 33, 201 ; from *Oesterr. Zeit. Berg u. Hüttenwesen*, 1898, 46, 41—46).—A manganese ore, consisting princi-

pally of psilomelane, is distributed over an area of 1000 × 500 kilometres in the Amazon district. The purer material occurs in layers with a smooth surface and a reniform structure on one side (anal. I). Other material encloses rock-forming minerals and has a rough surface (anal. II.) with sometimes the appearance of a sandstone (anal. III.)

	MnO.	BaO.	Insol. in HCl.	SiO ₂ .	Al ₂ O ₃ , Fe ₂ O ₃ .	Total.	Sp. gr.
I.	65·73	15·58	6·25	—	—	87·56	3·83
II.	32·05	6·32	55·13	—	—	93·50	3·28
III.	29·14	4·70	—	53·16	5·77	92·77	3·21

L. J. S.

Tin Ores from Banca and Billiton. By RICHARD BECK (*Zeit. Kryst. Min.*, 1900, 33, 205—206; from *Zeit. prakt. Geol.*, 1898, 121—127).—Cassiterite occurs in the islands of Banca and Billiton, Malay Archipelago, as an original constituent in granite, in quartz-veins traversing granite, and in alluvial deposits. A small amount of tin occurs as silicate in the minerals of the granite. The cassiterite in the quartz-veins has probably been collected from the surrounding rock by thermal waters, as is suggested by the occurrence of tin oxide in a siliceous sinter deposited by a warm spring in Selangor. Analysis of this siliceous sinter gave,

SiO ₂ .	H ₂ O.	SnO ₂ .	Fe ₂ O ₃ .
91·8	7·5	0·5	0·2

L. J. S.

Marbles. By J. H. L. VOGT (*Zeit. Kryst. Min.*, 1900, 33, 203—204; from *Zeit. prakt. Geol.*, 1898, 4—16, 43—52).—A detailed discussion from various points of view of marbles (including dolomitic marbles). Several analyses are given.

L. J. S.

Phosphorite [from North Germany]. By W. KOERT (*Zeit. Kryst. Min.*, 1900, 33, 199; from *Jahrb. Preuss. geol. Landesanst.*, for 1898, 1900, 19, cxlvi—cxlix).—Boulders of a middle Miocene rock in the neighbourhood of Tesperhude, below Lauenburg on the Elbe, contain dark brown phosphorite nodules in association with molluscan shells. The nodules consist of sandstone with phosphorite as a cementing material, showing a concentric structure round each quartz-grain. Analysis by Klüss gave I for the rock and II for the nodules. The phosphorite has originated by concentration, around shells, from the surrounding rock.

	Fe.	CaO.	CO ₂ .	P ₂ O ₅ .
I.	2·75	21·17	17·39	0·46
II.	2·84	21·64	3·82	12·73

The remainder consists of silica (quartz and combined silica), water and organic matter, together with traces of aluminium, magnesium and potassium; fluorine is absent.

L. J. S.

Analyses of Minerals from the Langesund Fjord. By HJALMAR SJÖGREN (*Bull. Geol. Inst. Univ. Upsala*, 1900, 4, 227—230).—Analyses by R. Mauzelius are given of minerals from islets in the

Langesund Fjord, Norway, of which crystallographic descriptions have recently been given by G. Flink (*ibid.*, 1899, 4, 16—27). Epididymite (Abstr., 1895, ii, 23) occurs on Lille Arøe associated with eudidymite, ægirite, &c.; analysis I agrees with the formula $\text{HNaBeSi}_3\text{O}_8$. Associated with it is albite (anal. II) of secondary origin. Diaspore from Övre Arøe, occurring as violet-blue scales in the interspaces between crystals of natrolite and also as implanted tabular crystals, gave the results under III (the Al_2O_3 includes traces of Fe_2O_3 and TiO_2).

	SiO_2 .	Al_2O_3 .	BeO.	Na_2O .	K_2O .	H_2O .	Total.	Sp. gr.
I.	72.04	—	10.22	12.66	0.27	4.51	99.70	2.55
II.	65.99	19.96	—	11.34	1.45	1.04	99.78	2.587
III.	0.21	84.38	—	—	—	15.70	100.29	3.35

L. J. S.

Hardystonite and Zinc-schefferite from Franklin Furnace, New Jersey. By JOHN E. WOLFF (*Zeit. Kryst. Min.*, 1900, 33, 147—151).—A new find of hardystonite (Abstr., 1899, ii, 435) consists of a large mass of almost pure material; this is greyish-white, and gave the analytical results under I. The refractive indices are $\omega = 1.6691$, $\epsilon = 1.6568$ (Na).

	SiO_2 .	Al_2O_3 .	Fe_2O_3 .	ZnO.	MnO.	CaO.	MgO.	K_2O .	Na_2O .	Ign.	Total.
I.	37.78	0.91	0.43	23.38	1.26	34.22	0.26	0.78	1.10	0.34	100.46
II.	52.86	1.08		3.38	5.31	24.48	13.24	—	—	0.45	100.80

Analysis II proves a pyroxene occurring as large, brownish-red platy masses to be a zinc-schefferite. There is a good parting parallel to the basal plane; sp. gr. 3.31. Optical determinations are given in an appendix by G. Melcher.

L. J. S.

Epidote and Zoisite. By PIERRE TERMIER (*Bull. Soc. franç. Min.*, 1900, 23, 50—64. Compare Abstr., 1896, ii, 568; 1899, ii, 303).—A case is described of the occurrence together of the trimorphous minerals epidote, α -zoisite and β -zoisite. The “green rocks” of Mount Pelvas (or Paravas) on the Franco-Italian frontier contain veins and patches of white prehnite in which are embedded prisms of pale green epidote (anal. I by F. Pisani) and fine needles of very pale rose-coloured zoisite (anal. II and III). The zoisite has the optical characters of α -zoisite, but sometimes a little β -zoisite is intergrown with it. At times there are also regular intergrowths of epidote and zoisite, with a definite crystallographic orientation between the two minerals; this indicates that the crystalline structures of epidote and zoisite must be closely related.

	SiO_2 .	Al_2O_3 .	Fe_2O_3 .	MnO.	CaO.	MgO.	K_2O .	Na_2O .	H_2O .	Total.
I.	37.62	28.50	9.30	—	23.20	trace	trace	trace	2.01	100.63
II.	41.44	31.67	0.35	trace	25.03	0.69	0.28	0.41	1.38	101.25
III.	40.92	31.80	0.39	trace	24.92	trace	trace	trace	1.69	99.72

L. J. S.

Chabazites from Sardinia, and from the Granulites of Striegau, Silesia. By CARLO RIMATORI (*Atti Real. Accad. Lincei*, 1900, [v], 9, ii, 146—151).—Analysis of chabazites from the granu-

lites of (I.) Maddalena and (II.) Striegau, and (III.) from the volcanic stone of Montresta give the following results :

	SiO ₂ .	Al ₂ O ₃ .	Fe ₂ O ₃ .	CaO.	K ₂ O.	Na ₂ O.	H ₂ O.
I.	48.66	18.32	2.18	5.47	1.56	4.64	19.17
II.	48.54	16.44	2.93	7.55	3.46	0.11	21.05
III.	47.96	22.51	—	6.27	2.96	trace	19.68

T. H. P.

A New Mineral from near Cassel. By MAX BLANCKENHORN (*Zeit. Kryst. Min.*, 1900, 33, 199 ; from *Jahrb. Preuss. geol. Landesanst.*, for 1897 ; 1900, 18, iii, 109—129).—In a description of the Muschelkalk in the neighbourhood of Cassel, the following analysis by Klüss is given of an apparently new mineral, honey-yellow to orange-red and yellowish-green in colour, from a sandy, friable oolite :

SiO ₂ .	Al ₂ O ₃ .	CaO.	MgO.	H ₂ O.	Organic matter.	Total.
20.71	31.17	1.99	0.07	45.59	0.42	99.95

L. J. S.

Altered Fayalite from the Granulites of Villacidro. By DOMENICO LOVISATO (*Atti Real. Accad. Lincei*, 1900, [v], 9, ii, 10—13).—In heterogeneous veins and nests in the Villacidro granulites are found small masses of a very dark mineral having a hardness between 5 and 6 and a density of 3.984 at 17.2°. Analysis (by C. Rimatori) :

SiO ₂ .	FeO.	Fe ₂ O ₃ .	MnO.	CaO, MgO, Na ₂ O.	Total.
28.61	17.55	43.09	8.83	1.09	99.17

This corresponds with the formula, 4Si₃O₉Fe₂.4Fe₃O₄.3MnO. It is concluded that the mineral represents an altered form of fayalite, which, however, contains 63.54—65.49 per cent. of ferrous iron, and never more than 5.07 per cent. of manganese.

T. H. P.

Meteoric Irons from Griqualand East, South Africa. By EMIL W. COHEN (*Ann. S. African Museum*, 1900, 2, 9—19).—The "Kokstad" iron in the Vienna Museum gave, on analysis by J. Fahrenhorst, the results under I. A larger mass (298 kilograms) supposed to be from Matatiela in the same district, which has been in the South African Museum since 1885, gave analysis II. Both are octahedral irons with lamellæ of medium width, but they show differences in structure which suggest that they do not belong to the same fall. It is proposed that the latter shall be known as the Matatiela iron.

	Fe.	Ni.	Co.	Cu.	C.	Cl.	P.	S.	Total.	Sp. gr.
I.	91.21	8.01	0.63	0.02	0.03	0.05	0.22	trace	100.17	7.7876
II.	92.20	7.30	0.67	0.03	0.08	0.03	0.19	0.03	100.53	7.8084

L. J. S.

Meteoric Iron from Bethany, Great Namaqualand. By EMIL W. COHEN (*Ann. S. African Museum*, 1900, 2, 21—29).—As there is some confusion in the various irons from South-West Africa, it is proposed to refer to the one often called the great Namaqualand iron (weight about 232 kilograms) as the Bethany iron. The etched

surfaces of this show two portions, one with the normal structure of a finely lamellar octahedral iron, and the other as broad homogeneous-looking bands. Analysis by J. Fahrenhorst of these two portions gave the results under I and II respectively. Sp. gr. 7.8502.

	Fe.	Ni.	Co.	Cu.	C.	Cr.	Cl.	S.	P.	Total.
I.	91.07	8.18	0.63	0.03	0.01	0.02	trace	0.04	0.06	100.04
II.	92.29	7.77	0.57	0.10					0.06	100.79

L. J. S.

New Meteorites from Allegan, Michigan, and Mart, Texas.
By GEORGE P. MERRILL and HENRY N. STOKES (*Proc. Washington Acad. Sci.*, 1900, 2, 41—68).—*Allegan*.—This stone fell at Allegan, Michigan, on July 10, 1899; the total weight was about 70 lbs. It is very friable; sp. gr. 3.905. Chondrules of olivine and of enstatite, sometimes broken and pitted, are set in a confused ground-mass of fragments of olivine and enstatite with metallic iron, troilite, and chromite. This agglomerated structure points to a tuffaceous origin of the meteorite. From analyses of the magnetic portion and of the stony portions soluble and insoluble in hydrochloric acid, the composition of the metal (23.06 per cent. of the whole) is given as; Fe, 91.42; Cu, 0.046; Ni, 7.87; Co, 0.66; Total, 99.996; and of the stony portion as:

SiO_2 .	TiO_2 .	P_2O_5 .	Al_2O_3 .	Cr_2O_3 .	FeO .	FeS .	MnO .	CaO .
45.42	0.10	0.35	3.31	0.69	11.02	6.57	0.23	2.24
		MgO .	K_2O .	Na_2O .	H_2O .	$\text{NiO, Li}_2\text{O}$.		
		28.60	0.30	0.86	0.31	traces		

The isolated chromite gave; Cr_2O_3 , 50.31; Al_2O_3 , 9.67, $\text{FeO}(\text{Fe}_2\text{O}_3)$, 28.78; MgO , 2.76; TiO_2 , 1.20.

Mart, Texas.—This iron was found in 1898 and originally weighed 15½ lbs. The structure is octahedral with very distinct Widmanstätten figures. Small amounts of schreibersite, troilite and chromite are present. Analysis gave:

Fe.	Ni.	Co.	Cu.	P.	S.	Cr, Fe_2O_3 .	Total.
89.68	9.20	0.33	0.037	0.158	0.017	traces	99.422

L. J. S.

Physiological Chemistry.

The Influence of Minimal Doses of Suprarenal Extracts on Blood-pressure. By BENJAMIN MOORE and C. O. PURINTON (*Pflüger's Archiv*, 1900, 81, 483—490).—The authors doubt whether the substances separated from the suprarenals are those which cause elevation of blood-pressure. They are less active than the raw extract, and such minute doses of the active physiological substance produce

an effect on blood-pressure that a very small contamination of an inactive substance by the active one will lead to positive effects.

The extract was made from the suprarenals of oxen by extracting them with 10 times their weight of water. This extract was freed from proteid by boiling after acidifying, and then diluted 1000-fold. A more active extract was obtained by precipitating with lead acetate, and subsequently freeing from lead in the usual way. The active substance is in the filtrate, not in the precipitate, and although the filtrate loses by such treatment 75 per cent. of the organic material in the original extract, it is much more active. The filtrate contains the chromogen, and loses its activity slowly on standing. The amount of organic material was estimated in the usual way. As small a dose as 2-millionths of a gram per kilo. of body weight will in the dog produce a considerable rise of blood-pressure. Smaller doses, down to 0.2-millionths, produce a slight rise of pressure, usually followed by a fall. In some animals, the fall was not seen. The question arises whether the fall is caused by another substance, but the probability is that one active substance will produce different effects with different doses.

W. D. H.

Changes in the Substances in the Blood which are Soluble in Ether. By RICHARD WEIGERT (*Pflüger's Archiv*, 1900, 82, 86—100).—The substances present in the blood corpuscles which are soluble in ether diminish in amount by remaining in the warm, although air is excluded. This diminution of the ether extract is accompanied by a rise in the amount of acids soluble in ether. The substance in the blood which is soluble in ether, but diminishes in this way, is not fat, as stated by Cohnstein and Michaelis, and the change should not be described as lipolytic. In the blood-corpuscles and in the blood-plasma, there appears also to be a chemical process which leads to an increase of the ether extract.

W. D. H.

Hydroxyl-ions of the Blood. By RUDOLF HÖBER (*Pflüger's Archiv*, 1900, 81, 522—540).—The alkalinity of the blood is determined by the amount of hydroxyl ions in it. These arise by the hydrolytic splitting of the alkali salts of the weaker acids, especially of carbonic acid. An estimation of the total quantity of these salts gives, therefore, no indication of the alkalinity of the blood. The alkalinity can only be estimated by methods which do not alter the chemical balance there present. It is measurable by electro-chemical methods, and can be calculated from the E.M.F. of a concentration chain for hydrogen ions, or for a chain of hydroxyl ions. The two methods give widely different results. This, however, does not depend on the variability of the dissociation constants of water, but on the fact that the hydroxyl ion chains behave in an irregular manner to the oxygen electrodes used. With hydrogen electrodes, the molecular concentration of hydroxyl ions in defibrinated ox-blood is about $0.1-10^{-5}$.

W. D. H.

Oxidation in Animal Tissues. By AN. K. MEDVEDEFF (*Pflüger's Archiv*, 1900, 81, 540—573).—The experiments recorded are limited to observations on the oxidising action of liver extracts on salicyl-

aldehyde. A previous auto-digestion of the extract for periods varying from 18 hours to 6 days makes no difference to its oxidising power. Oxidation is therefore the result of the interaction of the aldehyde and the active material (oxidation-ferment) in the extract. This action is proportional to the square root of the concentration of the aldehyde, and directly proportional to the concentration of the ferment. It is proportional to the square root of the concentration of the aldehyde, because this is the proportion of that substance which is dissociated in solution. This idea is worked out in great detail and at considerable length, and theoretical views put forward to explain the action of oxidising ferments in particular, and all ferments in general.

W. D. H.

Composition of the Fat of Human Chyle. By FRANZ ERBEN (*Zeit. physiol. Chem.*, 1900, 30, 436—452).—The fat in the urine in a case of chyluria was investigated. This is regarded as equivalent to chyle fat. The following figures give the chief results. Elementary analysis: C, 76·52—76·59; H, 11·88—12·11; O, 11·37—11·55 per cent.; specific gravity, 0·905—0·92 at 15°; melting point, 44°; solidification point, 26°; acid number, 3·508; saponification number, 199·579; ether number, 196·071; Reichert-Meissl number, 2·254; Hehner number, 94·92; iodine number, 54·42; melting point of insoluble fatty acid, 44°.

The fat contains:—Free fatty acids, 1·680; neutral fats, 95·987; lecithin, 0·500; cholesterol, 1·715; glycerol, 10·717; total fatty acids, 95·573; soluble fatty acids, 0·65; insoluble fatty acids, 94·92 per cent. The insoluble fatty acids consist of oleic acid, 58·4; hydroxystearic acid, 6·6; stearic acid, 25·0; palmitic acid, 9·0; myristic acid, 1·0.

W. D. H.

The Properties of Nerve under the Influence of Certain Poisons. By NICOLAI E. WEDENSKI (*Pflüger's Archiv*, 1900, 82, 134—191).—The main properties of nerve investigated were excitability, conductivity, and action-current. The last was detected either by the telephone or galvanometer. Tracings were also taken of the attached muscle. A certain stretch of the nerve was subjected to the local action of certain poisons in solution (cocaine, chloral hydrate, phenol, and chloralose). There is stated to be complete parallelism between the alterations produced of the functional properties of nerve and those in its action-current. Some exceptions to this rule noted in the case of chloralose are only apparent and are due to the extraordinarily rapid return of function which occurs when the action of the poison is suspended.

W. D. H.

Action of Certain Ions on Ventricular Muscle. By D. J. LINGLE (*Amer. J. Physiol.*, 1900, 4, 265—282).—The experiments were performed with strips of the turtle's ventricle, and the results of Loeb's experiments on rhythmic contraction of striped muscle, and gonionemus tissue apply very closely to cardiac muscle. Sodium and not calcium is the stimulus for its rhythmic action, but a pure sodium chloride solution is injurious at last; calcium and possibly potassium salts improve the rhythm by neutralising this injurious

action. Heart-strips will not beat rhythmically in solutions of non-conductors like sugar and glycerol. W. D. H.

Origin of Glycogen From Proteid. By BERNHARD SCHÖNDORFF [with HEINRICH OFFERGELD] (*Pflüger's Archiv*, 1900, 82, 60—85).—The question whether glycogen can originate after feeding on a diet free from carbohydrates has been frequently investigated, but a critical examination of these researches from those of Claude Bernard's onwards shows that not a single one is conclusive. Either glycogen might have remained over in spite of the previous starvation period, or the diet employed (meat, &c.) was not free from carbohydrate. In the present experiments, frogs were used, and casein was the diet given to them; the result is stated to show with absolute certainty that no glycogen originates from a proteid which does not contain a carbohydrate group. W. D. H.

Can the Whole of the Glycogen Present in an Organ be removed by Sufficiently Long Extraction with Boiling Water? By JOSEPH NERKING (*Pflüger's Archiv*, 1900, 81, 636—640).—Calf's liver was repeatedly extracted with boiling water until the wash waters were absolutely free from glycogen. The residue was then extracted with dilute potash, when more glycogen was obtained. In the two experiments recorded, the amount of glycogen which was not extractable by water was respectively 24.9 and 76.4 per cent. of the total quantity present. This confirms the view that the glycogen which can be extracted by water is free in the organ, whilst that which cannot, is in chemical combination. W. D. H.

Origin and Excretion of Oxalic Acid. By ERNST SALKOWSKI (*Chem. Centr.*, 1900, ii, 131—132; from *Berlin. klin. Woch.*, 37, 434—437).—The source of oxalic acid is not proteid, for increase of proteid food (casein) does not produce a rise in oxalic acid excretion, and the acid is not formed from proteid during tryptic or bacterial activity. Calcium oxalate is constantly found in the fæces, and in not unimportant quantities in the bile. The source of oxalic acid is uric acid, and so, indirectly, nuclein; the acid is formed by a process of oxidation. Whether the seat of action is the liver was the subject of some experiments which did not yield satisfactory results. The subject of alimentary oxaluria is also discussed. W. D. H.

Solubility of Uric Acid in Nucleic and Thymic Acids. By MOTONOSUKE GOTO (*Zeit. physiol. Chem.*, 1900, 30, 473—477).—A fuller account of experiments previously published (this vol., ii, 421). W. D. H.

Absorption of Free Oxygen by Normal Urine. By MARCELLIN P. E. BERTHELOT (*Compt. rend.*, 1900, 131, 547—552).—Normal urine slowly absorbs oxygen from the air in quantity varying from 8 c.c. to 20 c.c. per litre of urine. There is no alteration in the quantity of urea present, in the proportion of dissolved carbon dioxide, or in the acidity, and the absorption of oxygen seems to be due to, or connected with, the colouring matters or leuco-

colouring matters of the urine. The fact that urine is a reducing agent although formed from arterial blood shows that the function of the kidneys is not purely mechanical. C. H. B.

Acidity of Urine. By MARCELLIN P. E. BERTHELOT (*Compt. rend.*, 1900, 131, 552—553).—The ratio of the acidity of urine as determined with phenolphthalein as indicator to that determined with litmus solution or litmus paper by the spot method, varies considerably. In one case it was 85 : 45, in another 52 : 16, and in another 126 : 14. These ratios are not affected by the absorption of oxygen by the urine. C. H. B.

Estimation of the Acidity of Urine. By OTTO NÆGELI (*Zeit. physiol. Chem.*, 1900, 30, 313—349).—An elaborate investigation by the use of numerous indicators of the various factors which make up the total acidity of the urine. W. D. H.

Excretion of Antipyrine by the Animal Body. By D. LAWROFF (*Ber.*, 1900, 33, 2344—2346).—Antipyrine was administered in doses of 4—10 grams per diem to a full-grown dog weighing 35 kilos. The urine contained a *glycuronic acid*, $C_{17}H_{20}O_8N_2$, of which the crystalline compound of the *barium* salt with barium chloride was analysed. M. O. F.

Hæmolytic Serums. By JULES BORDET (*Ann. Inst. Pasteur*, 1900, 14, 257—296).—The action of hæmolytic serums varies considerably with the kind of animal employed, but in the same serum the alexin which causes destruction of bacteria is identical with the hæmolytic substance. The stomata of the corpuscles manifest towards such alexins a fixative power which is compared with what is seen in the case of staining reagents. It is possible to prepare an antitoxin antagonistic to hæmolytic serum; this is anti-hæmolytic and anti-bactericidal. The action between the two substances appears to be that of chemical neutralisation. W. D. H.

Anti-hæmatic Serums. By PIERRE NOLF (*Ann. Inst. Pasteur*, 1900, 14, 297—331).—A number of experiments on the subject of agglutination are presented, and the mechanism of the process discussed. Mixture of the serum of one animal with that of another often produces a precipitate, but the precipitating agent is not regarded as the agglutinating substance. W. D. H.

Cytotoxins. By ÉLIE METCHNIKOFF (*Ann. Inst. Pasteur*, 1900, 369—377).—**Hæmolytic Serum and Red Corpuscles.** By J. CANTACUZÈNE (*ibid.*, 378—389).—**Leucotoxin.** By BESREDKA (*ibid.*, 390—401).—**Action of Hæmatoxin on Man.** By ÉLIE METCHNIKOFF and BESREDKA (*ibid.*, 402—414).—The term cytotoxin is introduced for those poisons of animal origin which act on the formed elements (cells, &c.) of organs. The best known example is that contained in serum. The practice of transfusion of an animal's blood into man has been abandoned because of the destruction of the red corpuscles so produced. The main experimental fact brought forward in this series of papers (which relate to the poisons which act, more or less specifically, on the red and white blood corpuscles respectively), is that small doses, instead of producing destruction of the corpuscles in question, act

in a stimulating way so as to lead to an increase in their number. This does not appear to be due to the development of an antitoxin.

W. D. H.

The Gonococcus and its Toxin. By J. DE CHRISTMAS (*Ann. Inst. Pasteur*, 1900, 14, 331—349).—The gonococcus in suitable media elaborates a toxin which, when applied in small doses to the cerebral tissues, produces rapid death. This gonotoxin is not dialysable, it is destroyed at 73°, and is precipitable by ammonium sulphate. If injected subcutaneously, an antitoxin is formed in the blood. The two substances neutralise one another both *in vivo* and *in vitro*. W. D. H.

Relationship between Chemical Constitution and Physiological Action. I. Physiological Action of Alkines of Piperidine. By CESARE PADERI (*Chem. Centr.*, 1900, ii, 588—589; from *Ann. Farm. Chim.*, 1900, 181—194).—The physiological action of piperylalkine and pipercolylalkine on frogs, rabbits, and dogs is similar to that of piperidine, whilst on the other hand, methylpipercolylalkine exercises a healing influence. Thus the introduction of glycol into the piperidine molecule has no effect on the physiological action, no matter whether the glycol replaces a hydrogen atom of the imino-group or a hydrogen attached to the closed chain. When, however, a hydrogen atom of the piperidine ring is replaced by glycol, and at the same time a hydrogen atom of the imino-group replaced by the methyl group, the physiological action is completely changed. E. W. W.

Chemistry of Vegetable Physiology and Agriculture.

Researches on the Formation of Acetic Acid by Bacteria producing Lactic Acid. By CHR. BARTHEL (*Centr. Bakt. Par.*, 1900, [ii], 6, 417—420).—The quantity of acetic acid produced during the lactic acid fermentation of milk varies only slightly with the conditions, the minimum being formed under those which are most favourable for the culture of the bacteria producing lactic acid. Acetic acid may be considered as a pathogenic product of these bacteria.

R. H. P.

Micro-organisms forming Dextran. By F. W. J. BOEKHOUT (*Centr. Bakt. Par.*, 1900, [ii], 6, 161—165).—A new species of *Streptococcus*, named by the author *S. hornensis*, has been isolated from curdled milk, some water samples, and flowers, and has the power of converting media containing up to 20 per cent. of sucrose into a slimy mass with the formation of dextran. Peptone is the most favourable source of nitrogen for the culture of these bacteria, which are capable of producing dextran even in the absence of oxygen.

R. H. P.

Schizomycetic Fermentation. By OSKAR EMMERLING (*Ber.*, 1900, 33, 2477—2479. Compare Abstr., 1899, ii, 569).—A 10 per

cent. solution of milk sugar, when treated with *Bacillus lactis aerogenes* in the presence of calcium carbonate and nutritive salts, becomes turbid and evolves hydrogen and methane ; at the same time, a slimy precipitate is produced consisting of a mass of viscid threads. In the presence of atmospheric oxygen the fermentation proceeds until a clear, viscid liquid is formed ; at this stage, the filtered solution, on the addition of alcohol, deposits a *galactan*, $C_6H_{10}O_5$; this substance, a white, tasteless powder, reduces Fehling's solution only after hydrolysis with dilute acids, and yields mucic acid on oxidation with nitric acid. Succinic acid is also a product of this fermentation.

Viscid substances are produced in the fermentation of galactose by this bacillus, but their formation is not noticed in the case of dextrose, the latter sugar yielding acetic and inactive lactic acids. Mannitol, under similar conditions, yields large quantities of alcohol and succinic acid, together with traces of the volatile acids. G. T. M.

Chemical and Biological Researches on the Preparation of "Sake." By YOSHINAO KOZAI (*Centr. Bakt. Par.*, 1900, [ii], 6, 385—405).—The preparation of "sake" can be divided into four stages, (i) preparation of the "koji" (the "malt"), (ii) preparation of the "moto" (the yeast), (iii) the fermentation, (iv) the clarification and pasteurisation. The enzyme of the "koji" (*Aspergillus oryzae*) forms dextrose from starch, dextrin, melitriose, sucrose, and maltose, but does not attack inulin or lactose ; 2 per cent. of alcohol acts injuriously on the enzyme, which is completely inactive in solutions containing 28 per cent. of alcohol ; as, however, during the whole process of the preparation of "sake" there is never more than 18 per cent. of alcohol present, this enzyme must be still active in the later stages of the process. In many samples of "koji" a white mould very similar to Lindner's *Sachisia suaveolens* and *Oidium lactis* is found ; it ferments sucrose, raffinose, dextrose, lævulose, or maltose, but not trehalose, rhamnose, lactose, or melizitose. The yeast of sake ferments sucrose, maltose, *d*-mannose, lævulose, dextrose, or methylglucoside very easily, trehalose or *d*-galactose with some difficulty, does not ferment lactose or rhamnose, and splits up melitriose into melibiose and lævulose. R. H. P.

Is the Formation of Enzymes a Trustworthy Characteristic of Yeasts ? By ALBERT KLÖCKER (*Centr. Bakt. Par.*, 1900, [ii], 6, 241—245).—The experiments of Dubourg (*Abstr.*, 1899, ii, 376) have been repeated and confirmed. The author disagrees with Dubourg's interpretation of these, and considers that the formation of enzymes is the most trustworthy characteristic of yeasts. R. H. P.

"Chinese Yeast" and the so-called *Amylomyces* (*Mucor Rouxii*). By CARL WEHMER (*Centr. Bakt. Par.*, 1900, [ii], 6, 353—365).—"Chinese yeast," a preparation used in East Asia for starting the fermentation of rice, contains a mould, *Mucor Rouxii*, which can be cultivated in solutions of lævulose, dextrose, galactose, sucrose, lactose, maltose, or inulin with peptone or ammonium nitrate, alcohol being formed in every case. R. H. P.

Nitrification in the Soil of Forests. By W. MIGULA (*Centr. Bakt. Par.*, 1900, [ii], 6, 365—370).—Nitrites and nitrates are not found except in minute quantities in the soil of forests. The author describes experiments in which such soil was inoculated with organisms which produce nitrites and nitrates. Nitrification did not take place in the upper layers, which contained decomposing leaves, but only in the deeper layers, zones of increasing intensity of nitrification being formed, which were different from the similar zones formed in arable land. The formation of nitrites, however, proceeded much more quickly in the cultures than the formation of nitrates.

R. H. P.

Occurrence and Action of Proteolytic Ferments in Germinated Seeds. By WL. BUTKEWITSCH (*Chem. Centr.*, 1900, ii, 386—387; from *Ber. deut. bot. Ges.*, 18, 185—189. Compare Green, *Abstr.*, 1887, 987, and Neumeister, *ibid.*, 1894, ii, 290).—The results of the author's experiments confirm those of Green (*loc. cit.*) in showing the presence in germinated seeds of a proteolytic enzyme which, like "animal trypsin," decomposes proteids with production of amides. An enzyme of this kind seems to be present in the axillary organs of seedlings of *Lupinus luteus*, and also (perhaps as zymogen) in ungerminated seeds of *L. angustifolius*.

Among the products of decomposition, substances were present which yield ammonia when boiled with dilute hydrochloric acid as in Sachsse's method for estimating asparagine or glutamine.

N. H. J. M.

Proteolytic Ferments of Germinating Seeds. By V. HARLAY (*Compt. rend.*, 1900, 131, 623—626. Compare this vol., i, 511, 576; ii, 35, 233, 301).—Germinating lentil seedlings are extracted with water and chloroform and the filtered extract tested with the tyrosinase derived from *Russula delicata*. The freshly-prepared solution remains colourless, but after a fortnight's digestion either alone or with casein, it gives a marked coloration, the liquid becoming red and then brown. If the solution is boiled before the addition of casein, the colour reaction is considerably diminished. It is found that the boiled solution has a solvent action both on the casein and the coagulated albumin.

These results point to the existence of tyrosine in the plant at the commencement of the experiment, a further quantity of this substance being formed during digestion at the expense of either the vegetable proteid matters or the casein. Hence the proteolytic ferment of the germinating lentil is analogous to the trypsin of animal tissues, since it gives rise to similar products during the digestion of proteids.

G. T. M.

Germination and Growth of Peas in Solutions of Salts of Fatty Acids. By OSKAR LÖVINSON (*Chem. Centr.*, 1900, ii, 344, and 388—389; from *Bot. Centr.*, 83, 1—12, and 33—43).—Instead of the usual nutritive solutions, the author employed solutions containing all the necessary bases in the form of formates, acetates, and propionates respectively. Nitrogen was present in the form of the

corresponding ammonium salt, sulphur as carbon disulphide, and phosphorus in the free state dissolved in water (1 : 50,000).

The results of the germination experiments showed that the salts of fatty acid retarded germination ; the percentage numbers of seeds which germinated were 77·5 in formates, 66·66 in acetates, and 10 in propionates. Carbon disulphide promoted germination, but somewhat influenced the subsequent development. Phosphorus only retarded germination slightly.

The solutions of formates and acetates (but not propionates) proved to be very favourable to the growth of fungi and bacteria.

N. H. J. M.

Germination and Growth of Peas in Solutions of Salts of Fatty Acids. By OSKAR LÖVINSON (*Chem. Centr.*, 1900, ii, 681—682 ; from *Bot. Centr.*, 83, 209—224).—The plants grown in solutions of [salts of] formic acid lived on an average 52 days, whilst those in solutions of acetic or propionic acid lived 28 and 17 days respectively. The injurious effects of the compounds seemed to be diminished by gradually accustoming the plants to stronger solutions. The plants after becoming inured to solutions of [salts of] formic acid would doubtless be able to assimilate mineral and organic nutriment provided that the strength of the solutions had been such as to prevent the emptying of the cotyledons ; this also applies to the other acids with certain limitations. The great length of life (80 days) and vigorous growth of plants grown in solutions of formates, prove that the plants are capable of obtaining their sulphur from carbon disulphide and of assimilating phosphorus directly, and that the alkalis and alkaline earths do not require to be present in the form of salts of mineral acids.

E. W. W.

Proteid Metabolism in Plants. By ERNST SCHULZE (*Zeit. physiol. Chem.*, 1900, 30, 241—312).—A large number of observations on the chemical composition of different parts of various plants at different ages are recorded. They are carried out on the lines of the author's previous work, and confirm the views he had advanced concerning proteid metabolism. The proportion between the amounts of proteid decomposition products (amino-acids, hexon bases, &c.), varies at different stages. The most marked change is a diminution in the quantity of leucine, tyrosine, and the simpler amino-compounds, and the simultaneous increase of asparagine, and in some cases glutamine also, as age advances. The theory that the proteids break up into asparagine and a carbohydrate is not confirmed. Asparagine appears to be easily utilised for proteid synthesis.

W. D. H.

Material for Plant Nutrition in Apples and Pears. By EDUARD HOTTER (*Chem. Centr.*, 1900, ii, 484—485 ; from *Zeit. landw. Vers. Wes. Ost.*, 1900, 583—585).—By suitably manuring fruit trees their lives are prolonged, and weak trees strengthened. Analyses of 20 kinds of apples and pears showed that for every 100 kilograms of fruit about 70 grams of nitrogen, 35 of phosphoric oxide, 170 of potassium oxide, and 14 of lime are withdrawn from the ground. Fresh apples yield about 0·336 per cent. of ash, and contain 0·076 of

nitrogen, whilst pears give 0.301 of ash and 0.069 of nitrogen; calculated on the dry substances, these data become, for apples, 2.24 and 0.47 per cent. respectively, and for pears, 2.01 and 0.46. The following analyses of the ash of apples and pears are quoted, the figures in brackets referring to the pears: SiO_2 , 1.08 (1.55); SO_3 , 2.49 (5.02); P_2O_5 , 10.42 (11.92); Fe_2O_3 , 1.18 (0.98); CaO , 4.22 (4.73); MgO , 3.71 (4.29); K_2O , 51.58 (52.88). E. W. W.

Myrosin. By THOMAS BOKORNY (*Chem. Zeit.*, 1900, **24**, 771—772).—The presence of myrosin in plant substances may be conveniently proved by observing whether the addition of potassium myronate to about 1 gram of the material triturated with 5 c.c. of water at 30—40°, and contained in a small stoppered flask, develops the odour of mustard-oil within the course of 48 hours. Myrosin was thus detected in the seeds (except where otherwise stated) of the following plants. An asterisk denotes that potassium myronate or a glucoside which yields mustard-oil is already present.

Cruciferae:—*Black mustard, white mustard, summer radish (*Raphanus sativus*), roots also, **Iberis amara*, **I. umbellata*, **I. semper-virens*, *scurvy grass (*Cochlearia* *off.*), *winter cabbage (*Brassica oleracea*), red, white, curly, and turnip cabbages, wallflower (*Cheiranthus cheiri*), summer-stock, and *watercress (*Nasturtium* *off.*).

Leguminosae:—Bean (*Phaseolus vulgaris*), lentil, pea, and vetch.

Umbelliferae:—Carrot (*Daucus carota*), tap-root, and parsley, root.

The following gave negative results, the part tested being mentioned:

Compositae:—Herbage of *Aposeris foetida*, seeds of *Artemisia dracunculus* (possibly present), and leaf of elecampane (*Inula helenium*).

Various:—Herbage of pæony and spurge (*Euphorbia cyperissias*), young fruit of lime, fruit and seed of maple, herbage and blooms of soapwort (*Saponaria* *off.*), *Borago salvia* *off.*, and *Campanula rotundifolia*, seeds of pine and sea-pine, the inflorescence, leaf and stem of houseleek (*Sempervivum tectorum*), vegetative part of stone-crop (*Sedum acre*), and a young rhubarb leaf, also the onion, leek, and ripe beans.

R. L. J.

Bitter Principles of Hops. By GEORG BARTH (*Chem. Centr.*, 1900, ii, 681; from *Zeit. ges. Brauw.*, **23**, 509—513).—A sample of commercial lupulin gave 18.27 per cent. of ash, 63.93 of material soluble in ether, and 36.07 of lupulin husks. The portion soluble in ether contained 0.18 per cent. of wax, 11.55 of α -resin, 43.31 of β -resin, 0.17 of ash, and 8.72 of fat, oil, γ -resin, &c. The portion insoluble in ether contained 15.31 of ash insoluble in hydrochloric acid, 2.75 of ash soluble in hydrochloric acid, 4.78 of proteid substances, 2.34 of pentosans, and 10.89 (by difference) of non-nitrogenous substances, tannins, fibres, &c. The substances extracted by ether or light petroleum did not contain nitrogen. The quantity of sand in commercial lupulin varies from 10.9 to 20.2 per cent. E. W. W.

Adlumia Cirrhosa—A New Protopine-bearing Plant. By JULIUS O. SCHLOTTERBECK (*Amer. Chem. J.*, 1900, **24**, 249—253; and *Ber.*, 1900, **33**, 2799—2801).—The root of *Adlumia cirrhosa* (climbing

fumitory) contains about 1 per cent. of protopine, whilst the leaves contain much less. Fumarine is probably identical with protopine, and since fumarine was discovered and named long before its discovery in opium by Hesse, the author is of opinion that the name protopine should be abandoned. E. G.

An Alcornoco Bark known commercially as Jaborandi, and Alcornoco Barks in general. By C. HARTWICH and E. DÜNNENBERGER (*Arch. Pharm.*, 1900, 238, 341—352).—A “jaborandi bark” imported from Venezuela in 1888, was found, by botanical examination, to belong in reality to a species of alcornoco; it contained 16·6 per cent. of tannin. Further, several varieties of alcornoco barks were examined botanically, and, to a certain extent, chemically. In particular, from a specimen of bark denominated *Cort. Alcornoco*, the alcornin of Biltz, Frenzel and Spirgatis was isolated. This melts at 205°, and has a specific rotation +33·83°; a number of its colour reactions are described. It has the formula $C_{22}H_{34}O$, and it yields a *monoacetyl* derivative; consequently, it is an alcohol of the nature of phytosterol, and is better named *alcornol*. C. F. B.

Astragalus Caryocarpus. By GEORGE B. FRANKFORDER (*Chem. Centr.*, 1900, ii, 484; from *Amer. J. Pharm.*, 72, 320—325).—The unripe fruit of *Astragalus caryocarpus* has a bitter taste, which is probably due to the presence of an alkaloid, whilst the ripe fruit, on the other hand, has a peculiar, sweet taste. From the latter, a disaccharose, *astragalose*, has been obtained in the form of a grey hygroscopic powder. It melts at 95—98°, reduces Fehling's solution, has a rotatory power $[\alpha]_D +38\cdot5^\circ$, and yields a phenylhydrazone melting at 186—188°. Analysis of the latter showed it to be a hydrazone of a hexose. The rotatory power and properties of the sugar are, however, easily affected by change of conditions.

A substance which contains nitrogen and gives the reactions of an alkaloid was also isolated from the plant extract. E. W. W.

The Sea-weed *Ulva Latissima* and its Relation to the Pollution of Sea-water by Sewage. By EDMUND A. LETTS and JOHN HAWTHORN (*Chem. News*, 1900, 82, 164—165).—*Ulva latissima*, or sea lettuce, contains C, 35·15; H, 5·27; N, 6·25; O, 37·96; ash, 15·37 (in which is S, 3·21; Fe, 2·20) per cent., and when fermented yields hydrogen, carbon dioxide, propionic, butyric, and, probably, acetic acids; later, the mass blackens from the ferrous sulphide formed, and hydrogen sulphide is disengaged. The weed abounds in polluted waters, and can thrive in and assimilate large quantities of nitrogen from sea-water charged with sewage and ammonia or nitrates; probably this is the cause of the high percentage of nitrogen in the plant. It is suggested that the presence of the weed in large quantities may perhaps be regarded as evidence of sewage contamination.

D. A. L.

Toxic Action of Acid Sodium Salts on *Lupinus Albus*. By LOUIS KAHLENBERG and ROLLAN M. AUSTIN (*J. Physical Chem.*, 1900, 4, 553—569).—The toxic powers of solutions of acid sodium salts and of acids are compared by means of determinations of the concentra-

tions of solutions in which seedlings of *Lupinus albus* will just live. The acid sodium salts exert a far greater toxic influence than would be expected from the concentration of the hydrogen ions, and the authors hence conclude that the dissociation theory is unsatisfactory in explaining the toxic action of these acid salts. L. M. J.

Digestibility of some Non-nitrogenous Constituents of certain Feeding Stuffs. By G. S. FRAPS (*J. Amer. Chem. Soc.*, 1900, 22, 543—552).—According to Ladd (*N. York Agric. Expt. Stat. Geneva Rep.*, 1889, 149), the sucrose and reducing sugars present in lucerne and mixed hay, wheat bran, maize, cotton seed, and linseed meals and oats are completely digested; in turnips fed with mixed hay the reducing sugars were completely digested, but of the sucrose only 78.7 per cent. was digested.

The results of the experiments now described showed that as a rule the sugars are completely digested. The examination of twenty-three samples of excrement obtained in digestive experiments showed that neither sucrose nor dextrose was present; some of the samples contained reducing substances, but these do not seem to be sugars.

The results of Stone's experiments on the digestibility of pentosans (*Agric. Science*, 7, 6) in various foods (grasses, hay, sugar-beet, wheat bran, &c.) indicated that the average digestibility is 60.3 per cent. (compare also Lindsay and Holland, *ibid.*, 8, 172).

The author has determined the total pentosans, and also the pseudo-pentosans (that is, the constituents of the crude fibre which yield furfuraldehyde) in several foods, and also their digestibility. From 0 to 21 per cent. of the pentosans consists of pseudo-pentosans, and in four out of five cases the pseudo-pentosans are less digestible than the pentosans of the non-nitrogenous extract.

Of the nitrogen-free extract, 53 to 15 per cent. consists of sugars and pentosans. In the case of cow-pea meal, maize bran, and rice bran, the remainder of the extract consists of starch, which is more digestible than the pentosans; in the case of timothy hay and crab-grass hay, the order of digestibility is sugars, pentosans, residue.

As regards the crude fibre, the pseudo-pentosans are less digestible than the residue. It seems probable that the crude fibre and undigested non-nitrogenous extract decompose in the intestines with production of gases, of soluble substances which are resolved, and of insoluble products which pass into the excrement and, being soluble in acid and alkali, appear in the analysis as non-nitrogenous extract. This would make the digestibility of the non-nitrogenous extract seem less, and that of the crude fibre greater than is actually the case.

Attention is called to the importance of determining sugar in foods, and especially in hay and cotton seed meal. The determination of starch and pentosans is also of more importance than that of the crude fibre. N. H. J. M.

Rye as Food. By WOLDEMAR VON KNIERIEM (*Chem. Centr.*, 1900, ii, 394—396; from *Landw. Jahrb.*, 29, 484—523).—Crushed rye in conjunction with clover hay only slightly increases the yield of milk, but the rye seemed to have no injurious effect on the cows. When cows receive sufficient fat (in oil cake), rye increases the yield

of milk rather more than oats ; the amount of fat in the milk was diminished by rye.

In experiments with sheep, it was found that with the exception of the non-nitrogenous extract, the constituents of rye are less digestible than those of oats ; the fat in rye is very slightly digested. Pigs consume rye very unwillingly after some time, and exclusive feeding with rye causes illness, from which, however, the pigs rapidly recover when fed with barley. Rabbits and poultry object to rye. Rabbits digest much of the non-nitrogenous extract, but not the proteids.

On the whole, rye may be advantageously employed for feeding if used with care, and in conjunction with sufficient digestible fat.

N. H. J. M.

Vetch Corn as Food. By WOLDEMAR VON KNIERIEM (*Chem. Centr.*, 1900, ii, 396 ; from *Landw. Jahrb.*, 29, 524—540).—Crushed vetches considerably increased the yield of milk, but diminished the amount of fat in the milk. No injurious effect was observed during six years.

Rabbits digested vetches well, and the constituents showed higher digestion-coefficients than those of the various cereals.

Pigs object to vetches alone, and soon cease to gain in weight. This is attributed mainly to the high amount of proteids.

As regards the taste of milk and butter, the results obtained with vetches were satisfactory ; no bitter taste was noticed. N. H. J. M.

Feeding Cows with Cane Sugar. By EBERHARD RAMM (*Bied. Centr.*, 1900, 601—602 ; from *Milch Zeit.*, 1899, 673).—As in the other feeding experiments (following abstracts), the cows received during each period : hay, 14 ; straw, 4·5 ; roots, 50 ; and brewers' grains 4 kilos. per 1000 kilos. of live weight. In addition, they received earth-nut cake and cane sugar respectively (6 kilos.). The rations contained the following amounts of digestible substances per 1000 kilos. live weight ; earth-nut cake ration : proteid, 4·12 ; fat, 0·93 ; and non-nitrogenous matters, 13·48. Sugar ration : proteid, 1·70 ; fat, 0·54 ; and non-nitrogenous matters, 15·65.

The sugar had no injurious effect on the health of the cows. As compared with earth-nut cake, it increased the live weight by about 1 per cent., diminished the yield of milk per day by 0·86 kilo., and the yield of milk fat and milk dry matter by 0·058 and 0·133 kilo. respectively.

N. H. J. M.

Feeding Cows with Maize Gluten. By EBERHARD RAMM (*Bied. Centr.*, 1900, 29, 600—601 ; from *Milch Zeit.*, 1899, 658).—The results of feeding experiments showed that, like maize bran (this vol., ii, 39), maize gluten, as compared with earth-nut cake increased the yield of milk. The percentage composition of the maize gluten was found to be as follows : nitrogenous matter, 35·90 ; fat, 1·85 ; non-nitrogenous extract, 31·80 ; crude fibre, 16·00 ; ash, 1·20 ; and water, 13·25.

N. H. J. M.

Feeding Cows with Malt-germ Molasses. By EBERHARD RAMM (*Bied. Centr.*, 1900, 29, 599—600 ; from *Milch Zeit.*, 1899, 641).—Under the conditions of the experiments, malt-germ molasses

was shown to be a suitable substitute for the same weight of earth-nut meal. The malt-germ molasses contained: nitrogenous matter, 14.60; fat, 3.85; non-nitrogenous extract, 47.15 (including sugar, 25.05; crude fibre, 4.40; ash, 6.35; and water, 23.05 per cent. (compare this vol., ii, 502).

N. H. J. M.

Non-saccharine Matter contained in Molasses. By EBERHARD RAMM and C. MOMSEN (*Chem. Centr.*, 1900, ii, 489; from *Milch Zeit.*, 1900, 433—436).—The effect of the non-saccharine portion of molasses when used as food was investigated by feeding five milch cows with the following series of foods. (1) Residual molasses containing about 41 per cent. of sugar; (2) the corresponding amount of raw sugar; (3) an equal quantity of raw sugar with the non-saccharine mud obtained in the process of removing sugar from molasses; (4) residual molasses as in (1). In addition to these, a good basal ration was used throughout the experiments. The molasses-mud was used as a substitute for the ash, nitrogenous and other non-saccharine components of the molasses. By making the fourth period like the first and using the same rations, the effects due to decreasing lactation were eliminated from the calculations. During the raw sugar period the milk was found to contain less fatty matter, whilst in the third period it increased by as much as 71 grams of butter fat per day per 1000 kilograms of body weight, and the milk had at this time the highest specific gravity. The quantity of milk remained about constant in the first three periods and then decreased.

E. W. W.

Beans. By TÁMAS KOSUTÁNY, RICHARD WINDISCH, E. VON HÉRICS-TÓTH, LADISLAUS VON SZÉLL and ADOLF FALTIN (*Landw. Versuchs-Stat.*, 1900, 54, 463—479).—Analyses are given of Hungarian and French beans (compare Ballard, this vol., ii, 174); the results indicate that the Hungarian beans are the more nutritive, containing more proteids and carbohydrates, and less cellulose than the French beans.

Bean oil, extracted by ether resembles olive oil in appearance. The oil, dried over sulphuric acid, has the following properties: Sp. gr., 0.9670; Hehner number, 78.5; Reichert-Meissl number, 2.46; Köttsdorfer number, 135.4; iodine number (Hübl), 119.9; refraction at 25° and 40°, 81.5 and 72.5 respectively. The oil contains fatty acid triglycerides, much lecithin and a good deal of sulphur.

N. H. J. M.

Cork Oak. By EMILIO TASSELLI (*Bied. Centr.*, 1900, 29, 615—617; from *Staz. sper. agrar. ital.*, 1899, 32, 209).—The results of analyses are given showing the amounts of ash, and of ash constituents, in the cork, wood, roots, leaves, and fruit of the cork-oak. As regards the fact that large amounts of nitrogen and mineral matter are taken from the soil and that no manure is required, the results of calculations are given showing that, notwithstanding the large amounts of cork and wood removed, only one-tenth of the total supply of the soil would be utilised in 1200 years.

N. H. J. M.

Hemp. By M. SAMOGGIA (*Bied. Centr.*, 1900, 29, 602—604; from *Staz. sper. agrar. ital.*, 1898, 31, 353).—Pot experiments are described

in which hemp was grown in ignited sand watered with (a) Nobbe's solution containing chlorine, and (b) Knop's solution containing no chlorine, but more nitrate than (a). In the first stages of growth, when the chlorine of the seeds sufficed, the plants watered with Knop's solution grew best, but subsequently they became unhealthy. The total weight of air-dried plants were (a) 28.5 and (b) 42.0 grams. The separated fibre contained (a) 90.149 and (b) 88.470 per cent. of dry matter of the following percentage composition :

	Organic matter.	Cellulose.	Crude fat.	Reducing sugar.	N.	Ash.
a.	91.43	53.36	2.02	3.90	1.658	8.57
b.	88.85	37.00	2.83	7.98	2.465	11.15

The ash contained (per cent.):

	K ₂ O.	CaO.	P ₂ O ₅ .	SiO ₂ .	Cl.
a.	36.27	15.62	9.67	5.95	1.38
b.	30.85	5.33	10.79	6.33	0.59

Müntz and Girard showed that application of chlorides increased the cellulose and diminished the ash and reducing sugar.

Maceration during six days did not cause loss of pentoses and pentosans.

N. H. J. M.

Cultivation of Parsnip. By HENRI GUÉPIN (*Ann. agron.*, 1900, 26, 476—477; from *J. Agr. prat.*, 1900, i, 527).—The yield of parsnip varies from 30,000 to 60,000 kilos. per hectare. The percentage composition is as follows: Dry matter, 15.3; nitrogenous matter, 1.4; fat, 0.2; non-nitrogenous extract, 11.6; and cellulose, 1.2. As regards feeding value, the results indicate that parsnip is superior to mangolds, turnips, and carrots.

As indicated by the composition of the ash, parsnip requires abundance of phosphoric acid, potash, and lime.

Parsnip is suitable for feeding horses, cows, and bullocks.

N. H. J. M.

Effect of Different Potassium Salts on the Composition and Yield of Potatoes. By THEODOR PFEIFFER (*Landw. Versuchs-Stat.*, 1900, 54, 379—385. Compare *Abstr.*, 1898, ii, 306).—A reply to Sjollema (this vol., ii, 305), in which the author shows that Sjollema's results are not opposed to, but confirm, his own, which indicated that the injurious action of "crude salts" was due to the presence of magnesia. Other results obtained by Sjollema lend support to the author's view that the different degrees of injury by potassium chloride on the yield of starch do not accord with the amount of chlorides found in the potatoes, but depend rather on the variety of the potato.

N. H. J. M.

Soil Investigations in the Tokay Wine District. By BÉLA VON BITTÓ (*Landw. Versuchs-Stat.*, 1900, 54, 337—348).—Determinations of carbon dioxide, from which the calcium carbonate is calculated, were made in a large number of Hungarian soils. The results, as well as descriptions of the physical properties of the soils, are given in tables.

N. H. J. M.

Practical Conclusions from [the Results of] Soil Analyses. By P. DOERSTLING (*Bied. Centr.*, 1900, 29, 586—588; from *Fühling's Landw. Zeit.*, 1899, 184).—The soils were extracted (1) for 24 hours with water at the ordinary temperature, (2) for 6 hours with water at 50—55°, (3) for 6 hours with water through which carbon dioxide was passed, and (4) for 24 hours with 5 per cent. citric acid. The samples were collected in the spring after autumn application of (A) dung and (B) green manure. The following percentage amounts of the total potash, calcium carbonate, and phosphoric acid were dissolved by the different solvents.

A. Farm-yard manure.				B. Green manure.		
	K ₂ O.	CaCO ₃ .	P ₂ O ₅ .	K ₂ O.	CaCO ₃ .	P ₂ O ₅ .
Total per cent.	0·1645	0·611	0·1198	0·2185	0·418	0·1552
Per cent. of total.	1. 15·0	3·8	21·7	13·5	6·9	15·0
	2. 22·9	8·4	34·1	15·5	13·1	12·8
	3. 23·9	20·9	31·4	18·7	24·4	21·3
	4. 64·4	76·6	46·4	65·0	72·7	38·2

Analyses are given of soil before and after the application of lime and green manure, both together and separately. The results accord in some cases, but not always, with the yields of crops.

Analyses of soils growing healthy and diseased roots showed that the disease was not due to deficiency of nutritive matters in the soil.

N. H. J. M.

Composition of some Manure-soils. By LEOPOLD KOURIMSKY (*Bied. Centr.*, 1900, 29, 595—597; from *Zeits. landw. Versuchsves. Oesterr.*, 1899, 2, 580).—In the north-west of Bohemia various deposits, derived, it is supposed, from ancient Celtic dwellings and cemeteries, are employed as manures. The following percentage results were obtained from three deposits in Postelberg:

	Stones.	Soil.	Water.	Loss on ignition.	N.	K ₂ O.	CaCO ₃ .	P ₂ O ₅ .
1.	7·1	92·9	4·00	7·44	0·168	0·687	5·52	1·408
2.	3·9	96·1	9·80	7·22	0·196	0·908	3·64	1·344
3.	—	—	8·35	6·23	0·134	0·54	15·50	1·20

The results of analyses of muds from ponds and rivers are also given.

N. H. J. M.

Manurial Experiments. By JOSEF HANAMANN (*Bied. Centr.*, 1900, 29, 591—594; from *Zeit. landw. Versuchsves. Oesterr.*, 1899, 2, 573).—From the results of 35 years' experiments in pots and beds, the conclusion is drawn that it is possible to obtain quite normal plants in pots, and that such experiments furnish results of practical importance.

The results of some vegetation experiments, which are given in detail, indicated that when loss of nitrate by drainage is impossible, the nitrogen left after the first year will increase the yield of barley considerably.

The analytical results show that the composition of the barley grown in pots was normal, whilst as regards the size of the grain and the

relation of grain to straw, no essential difference was observed in the pot plants as compared with those grown in the field.

N. H. J. M.

Manurial Experiments with Vegetables. By RICHARD OTTO (*Bied. Centr.*, 1900, 29, 588—591; from *Gartenflora*, 1899, 48, 563).—Lettuce. The best results as regards yield and quality were obtained with farmyard manure. Sodium nitrate and kainite, both separately and mixed, do not seem favourable to the production of solid heads.

The order of yield in the case of kohlrabi, after the various manures, was (1) farmyard manure, (2) compost, (3) sodium nitrate and superphosphate, (4) sodium nitrate and kainite, (5) sodium nitrate, superphosphate and kainite, and (6) sodium nitrate. Non-nitrogenous manures alone did not greatly increase the yield as compared with the unmanured plot. Analyses of the plants obtained under the influence of the various manures are given. The percentage of nitrogen in the dry matter varies from 3 (without manure and with superphosphate alone) to 5.42 (with farmyard manure). The ash contained K_2O , 27.61 to 44.33; CaO , 8.84 to 12.32; and P_2O_5 , 12.80 to 16.26 per cent.

N. H. J. M.

Distribution of Manures. By BERTHAULT (*Ann. Agron.*, 1900, 26, 417—430).—In 1884, a field which had been manured with 30,000 kilos. of farmyard manure per hectare received in addition 200 kilos. of sodium nitrate. On one portion of the land the nitrate was sown broadcast and on two other portions it was distributed along the furrows, and in holes 40 cm. apart along the lines. The yield of roots on the three portions of the field was as follows: Nitrate sown broadcast, 21,785; in the furrows, 38,392; and in holes, 40,337. Whilst the localisation of manures must depend on the nature of the manures themselves and on the crop, it is thought that the system may be generally adopted with advantage (compare Schloësing, *Abstr.*, 1893, ii, 141).

N. H. J. M.

Methods of Experiments on the Preservation of Farm-yard Manure. By THEODOR PFEIFFER, F. MOSZEIK, and OTTO LEMMERMANN (*Landw. Versuchs-Stat.*, 1900, 54, 349—378).—The conflicting results hitherto obtained in experiments on the preservation of stable manure are, at any rate in part, attributed to imperfect methods. The method now proposed is based on the fact that the nitrogen supplied in the food is completely recovered in the excrement after deducting the amount deposited in the body and that of the milk wool, &c. The composition of the food and of the materials used for litter is therefore determined, as well as the composition of the faeces, urine and milk. By determining ash constituents (phosphoric acid and potash), the amounts of which remain of course unaltered, it is possible to ascertain how far the nitrogen results can be depended on. An important point which has to be considered is the extent of the loss of nitrogen in the manure before it is removed from the stalls (compare Müntz and Girard, *Compt. rend.*, 1892, 115, 1318, and 116, 108).

As regards the foods to be employed, mangolds and lucerne are to be

avoided. The authors propose meadow hay, dried beetroot sections and crushed earth-nut cake, with straw for litter. The whole quantities of hay and straw required for the experiment are prepared beforehand and sampled.

After describing the stalls and the arrangements for the solid and liquid manure, the sampling of the manure, and the analytical methods employed, the authors give in tables a number of results which show that the taking of samples can be made sufficiently accurate and that the feeding of the animals and the collection of the products can be conducted without loss.

N. H. J. M.

Street-dust as Manure. By ADOLFO CASALI (*Bied. Centr.*, 1900, 29, 583—586; from *Staz. sper. ital. agrar.*, 1898, 31, 377).—Street-dust is recommended as manure by Strabo, Pliny, and Columella, and it was highly valued during the middle ages. The results of analyses of a sample of sifted street-dust collected during a dry September show that the material is suitable for soils poor in lime. It is also of use for the purpose of mixing with nitrogenous manures, both as a diluent and to enable them to be uniformly distributed; in the case of superphosphate, street-dust would be of use in diminishing the acidity.

The author considers that street-dust is also of use in supplying a great variety of microbes, derived partly from rain and partly from excrementitious matters.

N. H. J. M.

Analytical Chemistry.

***p*-Nitrophenol as an Indicator.** By LEOPOLD SPIEGEL (*Ber.*, 1900, 33, 2640—2641. Compare Langbeck, *Chem. News*, 1881, 43, 161, and Wieland Abstr., 1883, 1167).—The author recommends a 2—5 per cent. alcoholic solution of *p*-nitrophenol in place of methyl-orange in ordinary acidimetry and alkalimetry. The change from yellow when alkaline to colourless when acid is very marked, and the indicator is quite indifferent towards carbon dioxide. Sodium ammonium phosphate and crystallised borax may be estimated by the aid of the same indicator, but not fused borax. J. J. S.

Wide Occurrence of Indicators in Nature. By G. S. FRAPS (*Amer. Chem. J.*, 1900, 24, 271—276).—The author has examined extracts of a large number of coloured flowers, leaves and fruits, and has found that, as a rule, the colouring matters are fairly sensitive as an indicator, giving one colour when acid and another when alkaline. E. G.

Abegg and Herz's Method for the Separation and Recognition of Acids. By WILHELM FRESSENIUS (*Zeit. anal. Chem.*, 1900, 39, 566—574).—With regard to Abegg and Herz's systematic scheme

(this vol., ii, 436), the author objects that the same necessity does not exist with acids, as with bases, to separate them one from another before they can be identified, and that many of the reactions used by Abegg and Herz are untrustworthy. For instance, neither cyanogen nor arsenious acid is precipitated by calcium chloride under the conditions defined. Tartaric acid is only precipitated completely by calcium chloride when time is allowed for it to crystallise. The precipitate is then very sparingly soluble in acetic acid, and may be easily mistaken for calcium oxalate. Calcium phosphate exhibits a similar behaviour with acetic acid. Boric acid finds no place in the scheme, and the difficulties resulting from the presence of silicates are not provided for. Other objections can be advanced to the methods advocated for the detection of the halogens and nitric acid, and on the whole the scheme has but little practical value. M. J. S.

Estimation of Potassium Perchlorate in Alkali Nitrates (Nitrate and Chili Saltpetre). By N. BLATTNER and J. BRASSEUR (*Chem. Zeit.*, 1900, 24, 767).—Five grams of the dried sample are mixed with 7 to 8 grams of pure calcium hydroxide and heated in a covered platinum or porcelain crucible for 15 minutes over a Bunsen burner. When cold, the mass is transferred to a measuring flask marked at 128 c.c. and extracted for an hour with water. After making up to the mark (3 c.c. is taken as the volume of the undissolved matter), the liquid is well shaken and filtered through a dry filter. One hundred c.c. (4 grams of sample) of the filtrate are carefully neutralised with dilute nitric acid using methyl-orange as indicator, and the chlorine is then titrated with silver nitrate as usual. After allowing for the percentage of chlorine present as chloride, the balance is calculated into potassium perchlorate. L. DE K.

Process for the Estimation of Chlorides, Chlorates, and Perchlorates in the Presence of each other By N. BLATTNER and J. BRASSEUR (*Chem. Zeit.*, 1900, 24, 793).—The chlorine as chloride is first estimated as usual. It is then again estimated after reduction of any chlorate by boiling with sulphurous acid and finally after ignition with calcium hydroxide (see preceding abstract).

The authors have not as yet found any chlorate in samples of saltpetre. L. DE K.

Estimation of Potassium Iodide. By THOMAS S. BARRIE (*Pharm. J.*, 1900, [iv], 11, 58).—When potassium iodide (5 grams in 20 c.c. of water) containing chlorides and bromides is treated with 5 per cent. solution of potassium dichromate (10 c.c.) and 10 per cent. sulphuric acid (10 c.c.), iodine alone is liberated. This is extracted with toluene or carbon disulphide, the solution shaken with a known volume of *N*/10 sodium thiosulphate solution and the excess titrated with standard iodine. R. L. J.

Simple and Accurate Method for Estimating the Dissolved Oxygen in Fresh-water, Sea-water, Sewage Effluents, &c. By EDMUND A. LETTS and ROBERT F. BLAKE (*Chem. News*, 1900, 82, 163–164).—An ordinary separating funnel is filled with the water to be examined and a measured volume withdrawn; a definite volume of

standard ferrous sulphate solution, containing about 48 grams per litre, is added, and then ammonia, the combined volume of these two reagents being equal to the volume of the water removed. The stopper is inserted with the exclusion of air-bubbles, and the liquids are mixed together. After 15 minutes, the funnel is inverted, the stem filled with a mixture of equal volumes of sulphuric acid and water, the tap opened, and when all the iron hydroxide is dissolved the solution is titrated with permanganate or dichromate.

D. A. L.

Estimation of Oxygen in Copper by Ignition in Hydrogen. By LEONARD ARCHBUTT (*Analyst*, 1900, 25, 253—262).—Blount (Abstr., 1896, ii, 333) has described a process based on the reduction of copper oxide by hydrogen. The sample is melted in a current of dry hydrogen and the water collected and weighed. The author whilst acknowledging the accuracy of this process prefers to estimate the oxygen by the loss in weight which the sample suffers when ignited in hydrogen as has already been proposed by Hampe. Thirty to forty grams of the copper, best in the form of bright turnings small enough to pass through a tube $\frac{1}{8}$ -inch in diameter, are thoroughly cleansed with ether, dried, and introduced into a dry weighed bulb tube, which is then reweighed. The whole is ignited for about an hour in a current of purified hydrogen, and then allowed to cool in the current. When cold, the hydrogen left in the bulb tube is displaced by dry air and the tube reweighed.

An illustration of the apparatus and bulb tube is given.

L. DE K.

Detection of Free Phosphorus. By P. MUKERJI (*J. Asiat. Soc. Bengal*, 1900, 69, ii, 97—101).—The author has noticed that hydrogen generated in contact with free phosphorus becomes phosphorescent.

The incompletely oxidised compounds of phosphorus yield, like phosphorus itself, a gas which burns with a green flame, but this is not luminous in the dark. The glow is lessened to some extent by the presence of much alcohol, ether greatly interferes with it, but is soon expelled, oil of turpentine stops it and should be first got rid of by washing the material with alcohol and then with water. Nitrous fumes, hydrogen sulphide, iodine, and oil of mustard in moderate quantities do not interfere.

The apparatus in its simplest form consists of a flask fitted with a tap funnel and a jet. Common zinc and dilute sulphuric acid are introduced, and after making sure that the reagents cause no glow, the suspected article is added and the effect observed in a dark room.

L. DE K.

Estimation of Phosphorus in Coke and Coal. By J. M. CAMP (*Chem. News*, 1900, 82, 8—9).—The coke, powdered to pass through a 40-mesh sieve, is dried at 100° for an hour, and when cool 5 grams are exposed in a porcelain crucible in a muffle overnight; the contents are, next morning, transferred to a platinum crucible, supported on a platinum tripod, on the top of the chimney of an Argand burner, and heated below boiling with 5 c.c. of dilute hydrochloric acid (1:2), and 10 c.c. of dilute hydrofluoric acid until dry,

further dried, but not baked, allowed to cool, and warmed with 15 c.c. of the dilute hydrochloric acid. The contents are transferred to an evaporating dish, boiled for one or two minutes with 5 c.c. of strong nitric acid, filtered, treated with 25 c.c. of strong ammonia, then with sufficient strong nitric acid to exactly dissolve the precipitate, after which 5 c.c. more is added. Precipitation with molybdate follows, &c., and 1.63 per cent. of the dried precipitate is taken as phosphorus.

D. A. L.

Estimation of Phosphorus in Ores, Pig-iron, and Steel containing Arsenic. By J. M. CAMP (*Chem. News*, 1900, 82, 9).—Five grams of pulverised dry ore are gently boiled for 30 minutes with hydrochloric acid, the solution diluted, filtered, and exposed on a steam-bath overnight. In the morning, 2 grams of pure oxalic acid and 50 c.c. of hydrochloric acid are added, the solution covered with a watch glass, taken to dryness sharply, but not baked, then, when cool, evaporated with 30 c.c. of strong hydrochloric acid until the first appearance of insoluble ferric chloride, treated with 10 c.c. of strong nitric acid, and when violent action has ceased, warmed to complete solution, diluted, and filtered into a flask, washing with 2 per cent. nitric acid. The portion of the ore insoluble in hydrochloric acid is ignited, fused with mixed carbonates, dissolved in excess of hydrochloric acid, allowed to dry overnight in a steam-bath, moistened with dilute hydrochloric acid and enough hot water to dissolve chlorides, warmed, filtered, added to the contents of the other flask, and the phosphorus determined in the whole, in the manner described in the preceding abstract. The method is applicable to the analysis of pig-iron and steel.

D. A. L.

Estimation of Phosphorus in Steel, &c. By FRED IBBOTSON and HARRY BREARLEY (*Chem. News*, 1900, 82, 55).—A solution of 2 grams of the steel in 45 c.c. of nitric acid of sp. gr. 1.2 is treated with permanganate until a pink colour or a precipitate of manganese dioxide persists on boiling; it is cleared with ferrous sulphate and after the addition of 4 c.c. of strong ammonia is shaken while hot with 30 c.c. of molybdate reagent, then kept at 70–80° for a few minutes, passed through a pulp filter, and washed. The precipitate is dissolved in ammonia, treated with 10 to 12 c.c. of hydrochloric acid and 10 c.c. of a solution of lead acetate (40 grams to the litre), heated and well shaken with a mixture of 10–12 grams of ammonium chloride and 50 c.c. of strong ammonium acetate solutions; the precipitate is filtered and weighed as lead molybdate. The process is applicable (with slight modifications) to pig-irons, nickel-steels and alloys, chromo-steels, tungsten-steels, spiegels and ferro-manganese (compare Abstr., 1899, ii, 337).

D. A. L.

Estimation of Phosphoric Acid as Phosphomolybdic Oxide. By H. C. SHERMAN and HENRY ST. JOHN HYDE (*J. Amer. Chem. Soc.*, 1900, 22, 652–658).—The solution representing 0.2–0.5 gram of the sample of phosphate is mixed with 25 c.c. of strong ammonia of sp. gr. 0.9; after neutralising with nitric acid, 5 to 8 c.c. of acid of sp. gr. 1.42 are added in excess. The solution is diluted to 150 c.c., heated to 50° and a 3 per cent. solution of ammonium molyb-

date slowly added with constant stirring until there are about 20 c.c. in excess. After 10 minutes, the liquid is decanted through a porcelain Gooch crucible, and the precipitate is washed thrice by decantation with 50—70 c.c. and then on the filter with 200—250 c.c. of cold 1 per cent. nitric acid. Finally, the precipitate is ignited by placing the crucible inside a nickel crucible and heating the bottom of the latter to a dull red heat for 15 minutes as directed by Woy (Abstr., 1898, ii, 138) and weighed as the oxide, $P_2O_5, 24MoO_3$. L. DE K.

Adulteration and Analysis of Arsenical Insecticides. By JOHN K. HAYWOOD (*J. Amer. Chem. Soc.*, 1900, 22, 568—582; 705—706).—The author calls attention to the adulterations of arsenical insecticides. These are readily detected by the usual methods.

As regards the *bonâ fide* articles they may be assayed as follows. Water may be determined in Paris or Scheele's green by drying for 12 or 15 hours at 100°. The total arsenious oxide is best estimated by the iodine process recommended by Smith (this vol., ii, 47). A good method for estimating copper in these substances is to titrate the iodine set free from potassium iodide in an acetic acid solution.

In order to completely extract free arsenious oxide from Paris green, a very large amount of water is necessary. The author finds that 500 c.c. of water dissolve an appreciable quantity of the arsenical copper compound, and that, therefore, the amount of free arsenious oxide found will be in excess of the truth (compare next abstract).

The amount of arsenious oxide, combined with the dissolved copper oxide, may be readily calculated from the amount of the latter. One part of copper oxide corresponds with 1.875 parts of arsenious acid.

A large number of analyses are communicated.

L. DE K.

[Estimation of] Free Arsenious Oxide in Paris Green. By EUGEN W. HILGARD (*J. Amer. Chem. Soc.*, 1900, 22, 690—693).—The author states that, on account of the slight solubility of octahedral arsenious oxide, the quantity of water used to dissolve the free arsenious oxide from 1 gram of Paris green should be raised to 600 or, preferably, 1000 c.c., and the extraction continued for 24 hours (compare preceding abstract.) The use of the microscope is recommended for the rapid detection of decided quantities of free oxide.

L. DE K.

Qualitative Test for Boric Acid. By E. M. WADE and M. L. WADE (*J. Amer. Chem. Soc.*, 1900, 22, 618).—About 0.1 gram of the substance to be tested for boric acid is put into a test-tube 2.5 cm. in diameter, and 20 cm. long; 0.5 c.c. of hydrochloric acid, and 10 c.c. of methyl alcohol are added, and the mixture is rapidly boiled down to a small bulk by moving the lower end of the tube in the flame of a burner, and holding the moistened end of a piece of turmeric paper just outside the mouth in contact with the evolved vapour. If boric acid is present, the turmeric will turn a characteristic red, which is coloured pink, or deep purple, or blue when moistened with very weak ammonia.

L. DE K.

Estimation of Potassium by Phosphomolybdic Acid. By WAVELET (*Chem. Centr.*, 1900, ii, 689—690; from *Ann. Chim. anal. appl.*, 5, 289).—The precipitate which sodium phosphomolybdate gives

with potassium salts contains potassium and phosphoric acid in the invariable ratio $K_2O/P_2O_5 = 1.99$, although the amount of molybdenum may vary. To prepare the reagent, 140 grams of sodium carbonate, 20 grams of ordinary sodium phosphate, and 70 grams of freshly ignited molybdenum trioxide are dissolved together in 500 c.c. of water, 200 c.c. of nitric acid are added, the solution made up to a litre and filtered after 24 hours. To estimate potassium, an excess of the reagent is added, the mixture evaporated to dryness, the residue rubbed to powder, heated with dilute nitric acid (1:10), and, after cooling, the precipitate collected and thoroughly washed with dilute nitric acid. The phosphoric acid in it is then estimated in the usual way with magnesia mixture, but the ammonium magnesium phosphate may be titrated instead of being ignited. It is dissolved in nitric acid, and the solution neutralised with ammonia; 1 c.c. of acetic acid and some sodium acetate are added, and then a standard solution of lead nitrate (35 grams per litre) until a drop gives a yellow colour with potassium iodide.

M. J. S.

Shortened Method for Estimating Potassium in its Salts. By HUGO NEUBAUER (*Zeit. anal. Chem.*, 1900, **39**, 481—502).—The following process, if strictly adhered to in every detail, gives an accurate estimation of potassium in a solution which may contain sodium, magnesium, calcium, chlorides, and sulphates: Twenty-five c.c. of the aqueous solution of the substance (0.5 gram) are mixed with a few drops of hydrochloric acid and a small excess of platinic chloride, and evaporated on the water-bath just to dryness. After cooling, the mass is moistened with 1 c.c. of water and well rubbed with a pestle made from glass rod; 30 c.c. of alcohol are then added in portions of 10 c.c. at a time, rubbing very intimately after each addition. After half an hour, the precipitate is transferred to an asbestos filter in a platinum Gooch crucible, and thoroughly washed with strong alcohol (93—96 vols. per cent.) and finally with ether. The contents of the crucible are next reduced by very gradual heating in hydrogen, or equally well in coal-gas (5 minutes below red heat and 20 minutes at a very dull red), and then thoroughly washed with hot water. The crucible is then filled with 5 per cent. nitric acid, which is allowed to act for half an hour, returning it as it slowly percolates through the filter. The reduced platinum is again thoroughly washed with hot water, dried, ignited, and weighed. Multiplication by 0.48108 gives the corresponding weight of potassium oxide. Should barium be present, the reduction must not be performed with coal-gas, but with hydrogen; with this exception, the process needs no alteration, and equally good results are obtained.

M. J. S.

Detection of Sodium Carbonate in Milk. By P. SÜSS (*Chem. Centr.*, 1900, ii, 596; from *Pharm. Centr.*, **41**, 465).—As little as 0.05 gram of sodium carbonate in 100 c.c. of milk can be detected by the rose-red coloration produced on adding a 0.2 per cent. alcoholic solution of alizarin.

M. J. S.

Estimation of Free Alkali in Soaps. By R. E. DIVINE (*J. Amer. Chem. Soc.*, 1900, **22**, 693—695).—The author has modified

Dudley and Pease's process, titration of the free alkali by means of $N/10$ alcoholic stearic acid, so as to avoid the troublesome filtration of the alcoholic solution of soap from any undissolved alkali carbonate.

Two grams of undried soap are introduced into a round-bottomed flask, 50 c.c. of alcohol and a definite number of c.c. of $N/10$ alcoholic stearic acid, more than sufficient to neutralise any alkali present, are added, and also a little phenolphthalein. After boiling for half an hour under a reflux condenser, the excess of stearic acid is titrated with $N/10$ alcoholic soda and the total amount of alkali calculated.

Another 2 grams of the sample are boiled with 50 c.c. of alcohol, a 10 per cent. solution of barium chloride is added in quantity just sufficient to decompose the alkali found, and the liberated barium hydroxide is then titrated with $N/10$ alcoholic stearic acid and phenolphthalein, the result being expressed as free alkali.

The difference between the two titrations represents alkali carbonate.

L. DE K.

New Volumetric Method for the Estimation of Silver. By LAUNCELOT W. ANDREWS (*Amer. Chem. J.*, 1900, 24, 256—266).—The process is a modification of the one introduced by Pisani for the estimation of very small quantities of silver by means of a solution of iodine containing starch.

The silver solution should contain not quite 5 per cent. of nitric acid and be free from mercury and the lower oxides of arsenic and antimony; any nitrous acid should be expelled by boiling, and sulphurous acid must be removed by addition of ferric sulphate. A solution of ferrous sulphate is added in such quantity that there shall be at least as much iron as silver, and an equal quantity of iron as ferric sulphate is also added; if the amount of silver should be more than 0.02 gram per 100 c.c., it is best to first convert the iron sulphates into nitrates by judicious addition of strontium or lead nitrate.

The starch-iodine solution is then run in from a burette until the colour of the liquid turns slightly blue, showing that all the silver is precipitated. This solution is best prepared by heating 9 grams of pure iodine and 50 grams of purified maize-starch with 100 c.c. of water in sealed tubes for an hour in a boiling water-bath. When cold, it is diluted to a convenient strength, say a $N/20$ or $N/100$ solution. This should be standardised with silver nitrate; estimation of the iodine by means of sodium thiosulphate would give erroneous results.

L. DE K.

Gravimetric Estimation of Zinc as Sulphate. By WILHELM EULER (*Zeit. anorg. Chem.*, 1900, 25, 146—154).—The estimation of zinc as sulphate is sufficiently accurate for ordinary work. The zinc solution, which must contain only sulphuric acid or acids which are volatile in the presence of sulphuric acid, is evaporated to dryness in a weighed platinum crucible and the residue cautiously heated at a dull red heat to constant weight. The result may be confirmed by decomposing the sulphate over the blow-pipe and weighing as zinc oxide.

E. C. R.

Lead and Cadmium Ferrocyanides. By EDMUND H. MILLER and HENRY FISHER (*J. Amer. Chem. Soc.*, 1900, **22**, 537—543).—The authors confirm Gay Lussac's statement that lead ferrocyanide always retains more or less potassium ferrocyanide from which it cannot be freed by washing. A number of experiments have shown that the amount of potassium increases with the acidity of the liquid, it being just the same whether there is an excess of lead or ferrocyanide. The results also agree closely with Low's statement (*Abstr.*, 1893, ii, 437) that a solution containing 10 grams of crystallised potassium ferrocyanide per litre equals 0.01 gram of lead per c.c.; Furman has stated that 16 grams should be taken, but this figure is no doubt based on the erroneous conclusion that the formula of lead ferrocyanide may be calculated from that of zinc ferrocyanide.

Cadmium ferrocyanide thrown down from an ammoniacal solution has a composition agreeing with Hermann's formula $\text{CdK}_2\text{Fe}(\text{CN})_6$, but when precipitated from an acid solution, its composition lies between that formula and the one proposed by Wyruboff, $\text{K}_5\text{Cd}_3[\text{Fe}(\text{CN})_6]_4$. This fact is also confirmed by Mackay (this vol., ii, 49), who states that it requires about 2.5 per cent. less potassium ferrocyanide to precipitate cadmium than would be required by the formula $\text{CdK}_2\text{Fe}(\text{CN})_6$. The results again contradict Furman's statement that the cadmium standard may be calculated from the zinc standard.

L. DE K.

Analysis of Lead and Tin Ores, also of the most important Lead and Tin Preparations, and their Commercial Products. By H. MENNICKE (*Chem. Centr.*, 1900, ii, 399; from *Zeit. öffentl. Chem.*, **6**, 227—235. Compare this vol., ii, 688).—Galena may be assayed by reducing 0.5 to 1 gram of the sample with 30 c.c. of dilute hydrochloric acid (1 : 3) and 1 gram of granulated zinc in a platinum basin. If a glass vessel is used, 2 grams of zinc must be taken. The reduced mass is collected on a weighed filter, dried and weighed; the lead is then extracted by means of dilute nitric acid, and the residual gangue weighed; the metal may, of course, also be estimated in the filtrate as sulphate.

Other lead ores and compounds may be assayed in a similar manner.

L. DE K.

Analysis of Lead and Tin Ores, also of the most important Lead and Tin Preparations and their Commercial Products. By H. MENNICKE (*Chem. Centr.*, 1900, ii, 594; from *Zeit. öffentl. Chem.*, **6**, 266).—Cassiterite cannot be completely dissolved by hydrochloric acid and zinc, so must be fused with soda and sulphur. The stannous tin in stannous chloride may be estimated by adding an excess of ferric chloride, and titrating the ferrous salt by permanganate; the total tin, by reduction with hydrochloric acid and zinc. Granulated tin is washed repeatedly with water, and then boiled with an excess of ferric chloride, or it may be dissolved in concentrated hydrochloric acid, precipitated with zinc, redissolved, oxidised with chlorate, and, after expelling chlorine, precipitated by ammonium nitrate. Tin-bronze, mosaic silver, mosaic gold, and similar products may be reduced with zinc and hydrochloric acid, noting that 2.2 milligrams of tin remain unprecipitated by zinc.

M. J. S.

New Volumetric Method for the Estimation of Copper. By SAMUEL W. PARR (*J. Amer. Chem. Soc.*, 1900, 22, 685—689).—The solution which contains the copper in the state of nitrate should also contain a small quantity (not exceeding 1 per cent.) of free nitric acid. The metal is now precipitated by heating on the water-bath and adding sulphurous acid and a slight excess of potassium thiocyanate. When the precipitated cuprous thiocyanate has completely subsided, it is collected on an asbestos filter and well washed. The asbestos is returned to the beaker and the whole heated to 70° with a few c.c. of 10 per cent. aqueous sodium hydroxide. Standard potassium permanganate is then added in amount sufficient to completely oxidise the cuprous oxide, shown by the liquid assuming a permanent green tint; excess of dilute sulphuric acid (1:5) is added, and when the liquid has become clear the titration is completed at 70°. Seven mols. of potassium permanganate represent 10 atoms of metallic copper. L. DE K.

Estimation of Copper Sulphate. By MARIO ZECCHINI (*L'Orosi*, 1899, 22, 372—376).—For the rapid valuation of copper sulphate for agricultural purposes, the author recommends a method based on the reduction of the salt by means of excess of sodium thiosulphate, the cuprous salt formed being then precipitated by ammonium thiocyanate and the excess of thiosulphate determined by titration with iodine solution. Details are given of the method, which gives results in good agreement with those obtained by electrolysis. T. H. P.

Volumetric Estimation of Corrosive Sublimate in Dressings. By F. URZ (*Chem. Centr.*, 1900, ii, 690; from *Pharm. Zeit.*, 45, 626).—The author modifies Lehmann's method (this vol., ii, 443) as follows: 100 c.c. of the solution, prepared in the usual way, are mixed with 5 to 10 c.c. of hydrogen peroxide and excess of $N/100$ alkali. The mixture is shaken, gently warmed, and the excess of alkali titrated. The reaction is $\text{HgCl}_2 + 3\text{H}_2\text{O}_2 + 2\text{KOH} = \text{Hg} + 2\text{KCl} + 2\text{O}_2 + 4\text{H}_2\text{O}$. Correction must be made for any acidity of the hydrogen peroxide. M. J. S.

Estimation of Aluminium. By EUGENE T. ALLEN and V. H. GOTTSCHALK (*Amer. Chem. J.*, 1900, 24, 292—304).—The precipitate obtained by decomposing sodium or potassium aluminate with carbon dioxide is a basic aluminium carbonate of approximately the composition $\text{OH} \cdot \text{AlCO}_3 \cdot 7\text{Al}(\text{OH})_3 \cdot 9\text{H}_2\text{O}$, contaminated with small quantities of alkali carbonate; the latter is completely removed on boiling with water containing a little ammonium chloride or nitrate, the precipitate changing in this process to the hydroxide. The latter, prepared in this way, is dense and can be filtered and washed much more rapidly than the hydroxide precipitated by ammonia. The following method of estimating aluminium is more rapid than the old one, whilst at least as accurate.

The substance is dissolved either in water or a mineral acid, in the latter case the excess of acid being nearly neutralised with ammonia; a solution of 1 to 2 grams of potassium hydroxide, in which the amount of silica, iron, and alumina is known, is then added until

the precipitate first formed is redissolved; an excess of alkali should be avoided. Carbon dioxide is then passed in until precipitation is complete, 20 minutes, as a rule, sufficing for 0.2 gram of alumina; the precipitate is for the most part transferred to a filter paper, washed with water, and then washed back into the original beaker, where it is boiled for 2 to 3 minutes with 150—200 c.c. of water containing a little pure ammonium chloride or nitrate. After settling, the precipitate is collected on a filter-paper, using a pump and cone, washed by decantation with hot water, burned, and, after heating for 10 minutes in the blowpipe flame, weighed; the hygroscopic nature of alumina renders it necessary to heat again, after the first approximate weighing, and weigh very rapidly.

The method is as accurate as the old one for iron and alumina occurring together, and, with a large proportion of the latter, is preferable; it is accurate in the presence of sulphates, whilst the old method gives high results. When, however, alkaline earths or lithium are present, it is not applicable.

W. A. D.

Estimation of Alumina as Phosphate in Ore and Blast-furnace Cinder. By J. M. CAMP (*Chem. News*, 1900, 82, 9—10).—A gram of the ore or cinder is treated for silica, and the cold hydrochloric acid filtrate is diluted to about 400 c.c. and treated with 30 c.c. of a 10 per cent. solution of ammonium phosphate and then with ammonia until a faint precipitate forms; 1.5 c.c. of strong hydrochloric acid are added, and for ores 50 c.c., for cinder 30 c.c. of a 20 per cent. solution of sodium thiosulphate. The mixture is heated to boiling, 8 c.c. of strong acetic acid and 15 c.c. of 20 per cent. solution of ammonium acetate are added, and the whole boiled for 10 minutes, allowed to subside, the clear solution decanted, precipitated, filtered, and washed on the filter with hot water 10 times, but not more, as aluminium phosphate is slightly soluble. The precipitate is ignited in a platinum crucible in front of the muffle until the paper chars, then finished in the hottest part; 41.85 per cent. of the weight is alumina.

D. A. L.

Relative Values of the Mitscherlich and Hydrofluoric Acid Methods for the Estimation of Ferrous Iron. By WILLIAM F. HILLEBRAND and HENRY N. STOKES (*J. Amer. Chem. Soc.*, 1900, 22, 625—630).—Mitscherlich's process, heating the ferruginous substances with a mixture of 3 parts of sulphuric acid and 1 part of water in a sealed tube from which the air has been expelled, gives utterly untrustworthy results in the analysis of ferruginous rocks when sulphides are also present. Owing to the high temperature, 160—200°, to which the tube is exposed, the sulphur is oxidised at the expense of any ferric oxide present and thus causes an apparent increase in the ferrous iron.

The hydrofluoric method is not affected by the presence of moderate quantities of sulphides.

L. DE K.

Estimation of Pyrrhotite in Pyrites Ore. By F. B. CARPENTER (*J. Amer. Chem. Soc.*, 1900, 22, 634—637).—Two grams of the sample, ground sufficiently finely to pass through a 100-mesh sieve, are boiled in a covered beaker with 30 c.c. of strong hydrochloric acid for

10 minutes; the insoluble portion is then collected on a weighed Gooch crucible, washed successively with warm dilute hydrochloric acid, hot water, and alcohol, and then repeatedly with small portions of carbon disulphide. After drying at 100° , the residue consisting of iron disulphide and silica is weighed and by deducting the amount of the latter, previously ascertained, the weight of the former is found. The sulphur present in the iron disulphide is subtracted from the total sulphur previously determined and the difference is calculated to pyrrhotite (Fe_7S_8). The presence of pyrrhotite may be ascertained by means of a magnet.

If zinc or copper sulphides are present in appreciable quantities an allowance must be made for the sulphur they contain. Zinc which is present as normal sulphide will be completely dissolved by the hydrochloric acid. Copper, however, may remain in the residue in the form of double copper iron sulphide (CuFeS_2) and its amount should be allowed for.

L. DE K.

Estimation of Cobalt in New Caledonian Ores. By THOMAS MOORE (*Chem. News*, 1900, 82, 66—67).—These ores consist mainly of hydrated oxides of manganese iron, aluminium, cobalt, and nickel, with relatively small proportions of calcium, magnesium, zinc, lithium, &c., and occasionally barium and copper. The cobalt only is determined, usually by electrolytic deposition or precipitation as ammonium cobalt phosphate. The ores contain from traces to 8 per cent.

In the author's method 2.5 grams of pulverised and dry ore are dissolved in hydrochloric acid, the solution evaporated to a syrup, and all soluble matter dissolved by adding water; 100 c.c. of a saturated solution of ammonium chloride are then added and the whole diluted to 400 c.c.; a solution of 1 part of strong ammonia in 15 of water is carefully but vigorously stirred in until the liquid becomes deep red, when 5 per cent. solution of sodium carbonate is dropped in until the liquid has only a slightly yellow tint. A further dilution to 500 c.c. follows, the whole being well shaken and filtered. Four hundred c.c. of the filtrate are heated to near the boiling point with 20 c.c. of saturated sodium acetate and 10 c.c. of acetic acid, and hydrogen sulphide is passed until nearly cold; the precipitate of cobalt, nickel, and zinc sulphides is filtered, washed with water containing hydrogen sulphide, dried, and ignited, then dissolved in hydrochloric acid with a little nitric acid, the latter being eliminated by twice evaporating with hydrochloric acid. The chlorides are dissolved in water, any iron removed by an emulsion of zinc oxide, the filtrate made up to 50 c.c., mixed with 10 to 15 c.c. of 10 per cent. hydrogen peroxide, then with 10 c.c. of 10 per cent. sodium or potassium hydroxide, boiled to remove excess of hydrogen peroxide, cooled, digested with potassium iodide and hydrochloric acid, and titrated with sodium thiosulphate (iodine $\times 0.46511 = \text{cobalt}$).

D. A. L.

Separation and Estimation of Small Quantities of Cobalt in the Presence of Nickel. By THOMAS MOORE (*Chem. News*, 1900, 82, 73).—The solution containing the chlorides of nickel and cobalt, after removal of any iron by means of zinc oxide and filtration, is diluted, heated nearly to boiling with a drop of hydrochloric acid,

then treated with bromine water and zinc oxide, boiled to expel most of the bromine, and filtered. The washed precipitate is stirred with a solution of hydrogen peroxide and sodium hydroxide, boiled to destroy excess of the peroxide, cooled, digested with potassium iodide and hydrochloric acid, and titrated with sodium thiosulphate, $I \times 0.46511 = \text{Co}$.
D. A. L.

Qualitative Separation of Nickel from Cobalt by the Action of Ammonium Hydroxide on the Ferricyanides. By PHILIP E. BROWNING and JOHN B. HARTWELL (*Amer. J. Sci.*, 1900, [iv], 10, 316—317).—The difficulties in F. W. Clarke's method (*ibid.*, 1894, [iii], 48, 67) of separating nickel from cobalt by precipitating as ferricyanides and extracting the nickel with strong ammonia, are caused by the passage of cobalt ferricyanide through the filter and by the separation of sulphur in the subsequent precipitation of the nickel with ammonium sulphide. The method works well, however, if a few drops of a solution of alum are added before precipitating the ferricyanides, and if the nickel is subsequently precipitated with sodium or potassium hydroxide; in this way, less than a milligram of nickel can be clearly detected.
T. M. L.

Separation of Cobalt and Nickel by means of Persulphates. By F. MAWROW (*Zeit. anorg. Chem.*, 1900, 25, 196—200).—According to the author's previous work (this vol., ii, 596), the separation of cobalt and nickel by means of persulphates, as described in Salomon and Coehn's patent (*Zeit. Elektrochem.*, 1900, 6, 43, 532), is not quantitative. In the case of the mixed salts of the two metals, the precipitate of cobalt oxide contains a small quantity of nickel and a small quantity of cobalt remains in solution, whilst if the mixed hydroxides are employed, they are both only partially converted into higher oxides, and on the addition of acids to the black precipitate both cobalt and nickel are dissolved.
E. C. R.

Analysis of Chrome-Iron Ore by the Borax Method. By R. W. EMERSON MACIVOR (*Chem. News*, 1900, 82, 97).—To prepare chrome-iron ore for analysis, the author strongly recommends Dittmar's process, which he describes as follows: 4 grams of a mixture of 3 parts of sodium potassium carbonate and 2 parts of borax, are fused in a platinum crucible, allowed to solidify, 0.5 gram of the ore (which must be ground to an impalpable powder) placed on the top of the mass, the whole fused with the lid on, then the crucible placed at an angle on the triangle, heated, and the contents stirred with a platinum wire for half an hour, allowed to solidify, and then fused again with 2.5 grams of sodium potassium carbonate. The mass is heated with water on a water-bath, filtered, and the chromates washed out.
D. A. L.

Analysis of Chrome and Tungsten Steels. By ALEXANDER G. M'KENNA (*Chem. News*, 1900, 82, 67—68).—The steel is heated with hydrochloric acid, and the evolved gas absorbed in a solution of ammonium cadmium chloride for the estimation of sulphur. The hydrochloric acid solution is heated with nitric acid, twice evaporated to dryness with hydrochloric acid, dissolved in the same acid, diluted, and the residue of tungstic acid and silica dried, weighed, and treated with hydrofluoric acid to remove silicon. It is then weighed again, fused with sodium carbon-

ate, extracted with hot water, and any residue of iron oxide weighed. The hydrochloric acid solution is concentrated, boiled with some nitric acid to drive off hydrochloric acid, and then with large quantities of the same acid and potassium chlorate; the precipitate is dissolved in hydrochloric acid, the solution treated with ammonia and ammonium acetate, and the manganese precipitated with bromine. The chromium is determined in the nitric acid solution by diluting and titrating with ferrous sulphate and permanganate. The phosphorus and carbon may be estimated in the usual way in separate portions of the steel. D. A. L.

Estimation of Molybdenum in Steel and Steel-making Alloys. By FRED IBOTSON and HARRY BREARLEY (*Chem. News*, 1900, 81, 269—271).—Steel, or ferromolybdenum, containing small proportions of molybdenum is dissolved in hydrochloric acid, in quantities of about 2 grams, and oxidised with nitric acid or potassium chlorate, the solution neutralised, or nearly so, with sodium carbonate, avoiding the formation of a red coloration or precipitate, and passed through a small pulp filter, which is then placed in a flask containing 2*N* sodium hydroxide to the extent of 30—40 c.c. in excess of that required to precipitate all the iron. When the filter is disintegrated, the contents of the flask are heated nearly to boiling, well agitated, fractionally filtered, acidified with hydrochloric acid, and the molybdenum precipitated as lead molybdate in the manner previously described (*Abstr.*, 1899, ii, 129).

The presence of molybdenum in steel does not affect the estimation of silicon, or of manganese when no large excess of ammonium acetate is used to precipitate the iron, or when six instead of three separate lots of chlorate are added in the volumetric method by oxidation with potassium chlorate in nitric acid solution; or of sulphur if the barium chloride is added to a distinctly acid solution; or of phosphorus if the long (acetate) method is followed, or in the rapid method when dissolving in ammonia and precipitating with magnesia mixture is adopted. Carbon in the residue obtained by treating the sample with copper solutions retains some molybdic oxide. In the presence of molybdenum, iron cannot be estimated gravimetrically, or by simple solution and titration, but reduction with sulphurous acid and titration with potassium dichromate or permanganate is effective. Nickel-molybdenum containing but little iron is dissolved in aqua regia, the solution poured into excess of ammonia, and the molybdenum precipitated from a portion of the filtrate, whilst the nickel is determined in another portion cyanometrically. If more than a few tenths per cent. of iron is present, a second precipitation is necessary, and the filtrates are mixed before determining the nickel and the molybdenum; with much iron, the molybdenum must be separated by means of sodium hydroxide as in the case of steels, and the nickel and iron separated afterwards in a fresh sample by means of ammonia.

Molybdenum powders have been found to contain metallic molybdenum and its oxide, tungsten and its oxides, silica, alumina, iron, ferric oxides, combined and free carbon, sulphur, and water. The total carbon and combined carbon may be determined in the usual manner, the molybdenum by heating carefully with sodium carbonate and potassium nitrate under sodium carbonate in a platinum crucible, over

a blowpipe, avoiding volatilisation of molybdenum as oxide, extracting with water, and precipitating with lead acetate, &c., as previously set forth (this vol., ii, 445). Methods are also suggested for determining the quantity of oxides present in the powder. D. A. L.

[Estimation of small quantities of Platinum in Gold.] By HEINRICH RÖSSLER (*Chem. Zeit.*, 1900, 24, 733—735).—See this vol., ii, 733.

Volumetric Estimation of Iodoform in Dressings. By MARTIN LEHMANN (*Chem. Centr.*, 1900, ii, 397; from *Pharm. Zeit.*, 45, 522—523).—The author has slightly modified his process (this vol., ii, 372.) Ten grams of the material are treated in a glass stoppered bottle with 200 c.c. of "Spiritus æthereus" for 24 hours at 20—25° with constant agitation; 20 c.c. of the solution are then treated as previously directed. L. DE K.

Testing Lemonade Essences. I. Essence of Lemon and of Bitter Orange. By NEUMAN WENDER and GEORG GREGOR (*Zeit. Nahr. Genussm.*, 1900, 3, 449—459).—The article is chiefly a review of the various methods in use for estimating the amount of alcohol and ethereal oils.

Alcohol may be estimated by Schade's salt process, but the authors prefer the method proposed by Hefelmann (*Abstr.*, 1897, ii, 605). In many cases, the simple determination of the sp. gr. of the sample answers the purpose. Ethereal oil is best estimated by a process communicated by Mann which consists in observing the diminution in volume, when the sample is diluted largely with water containing a little sulphuric acid, and then shaken with light petroleum.

The solubility of the essences in water is determined by the authors as follows. One c.c. of the sample is put into a tall graduated cylinder and water at 17.5° is gradually added with constant shaking until a perfectly clear solution is obtained.

Admixture of oil of lemon or bitter orange or of citral may be detected by the lessened solubility in water, and the polarisation of the petroleum extract. Vanillin may be isolated by evaporating off the alcohol, adding lead acetate, and shaking the filtrate with ether. The vanillin is then removed by shaking with dilute ammonia, the liquid is acidified with hydrochloric acid, and the vanillin again extracted with ether; finally, the phloroglucinol test is applied. L. DE K.

Separation of Oleic Acid from other Unsaturated Acids. By K. FARNSTEINER (*Zeit. Nahr. Genussm.*, 1900, ii, 3, 537—539. Compare *Abstr.*, 1899, ii, 705).—A reply to Lewkowitsch (this vol., ii, 376). L. DE K.

Estimation of Lactic Acid in the Commercial Article. By FERDINAND JEAN (*Chem. Centr.*, 1900, ii, 692; from *Ann. Chim. anal. appl.*, 5, 285).—Commercial lactic acid contains mineral acids, oxalic acid, volatile organic acids, and various salts. A known quantity is freed from volatile acids by repeatedly evaporating with water, then boiled with barium carbonate, and the filtered solution

evaporated and gently ignited. The barium carbonate in the ash is thoroughly washed, dissolved in a known excess of standard hydrochloric acid, and the excess titrated back 1 c.c. of *N*/10 acid = 0.009 gram of lactic acid. M. J. S.

Detection and Estimation of Acetoacetic Acid in Pathological Urine. By V. ARNOLD (*Chem. Centr.*, 1900, 345—346; from *Centr. inn. Med.*, 21, 417—423).—The characteristic test for acetoacetic acid with diazoacetophenone described by the author (this vol., ii, 113) is best applied to urine previously decolorised with animal charcoal. All samples which give Legal's acetone reaction also give a positive diazoacetophenone test. Ehrlich's *p*-diazobenzenesulphonic acid cannot be used instead. Salts of acetoacetic acid differ from ethyl acetoacetate in their behaviour with the latter reagent; they cause a light yellow colour, which turns deep red or dark purple on adding ammonia, whilst the ester gives an orange-red colour changed to pure red by ammonia. On the other hand, when using the author's reagent, the ammoniacal solution of salts of acetoacetic acid is brownish-red with a similarly coloured precipitate, and that of ethyl acetoacetate vermilion-red with a similarly coloured, finely granular precipitate. The precipitates are soluble in strong hydrochloric acid, with a purple-violet colour. If the freshly prepared solution of diazoacetophenone is so much diluted that addition of ammonia does not cause a yellow coloration and a salt of acetoacetic acid is then added, a passing yellow coloration is observed gradually turning into a dark purple violet, which, after a few minutes, fades and turns yellow again; ethyl acetoacetate gives at once a reddish-yellow coloration.

According to the author, acetone does not pre-exist in urine; the reaction obtained is due to acetoacetic acid. L. DE K.

Estimation of Potassium Hydrogen Tartrate in Wine. By LOUIS MAGNIER DE LA SOURCE (*Chem. Centr.*, 1900, ii, 692; from *Ann. Chim. anal. appl.*, 5, 281).—In attempting to estimate the potassium hydrogen tartrate by Berthelot and Fleurieu's method (precipitation by a mixture of alcohol and ether), complete precipitation is not obtained unless there is an excess either of tartaric acid or of a potassium salt. The author recommends that the latter should be added in the form of potassium bromide, of which a large excess is not injurious. M. J. S.

Estimation of Malic Acid. By ALBERT HILGER (*Chem. Centr.*, 1900, ii, 597—598; from *Verh. Vers. Deut. Naturf. und Aerzte*, 1899, 668).—Malic acid precipitates metallic palladium (0.294 gram of metal per gram of acid) from neutral or feebly alkaline solutions of palladium chloride. Glycerol and glycollic acid have the same effect, but tartaric, citric, succinic, and oxalic acids have no action. To estimate malic acid in wine, the alcohol and volatile acids are distilled off, colouring matters and tannic acid removed by charcoal, and the fruit acids then precipitated by basic lead acetate. The precipitate is dissolved in acetic acid, and the lead removed by a small excess of sodium carbonate; a 2 per cent. solution of palladium chloride is added, and then sodium carbonate to exact neutrality; the palladium separates

on shaking. The mixture is feebly acidified, heated for $1\frac{1}{2}$ hours on the water-bath, and the metal collected and dried. Tartaric acid reduces platinic chloride, malic acid does not. M. J. S.

Uric Acid and Purine Bases in the Blood and Animal Organs. By WILHELM HIS, jun., and W. HAGEN (*Zeit. physiol. Chem.*, 1900, 30, 350—383).—The estimation in the blood and extracts of organs of uric acid and the various purine bases is difficult on account of the proteid present. The precipitation of guanine with ammoniacal silver solutions is hindered by small quantities of albumose; if large quantities are present, they are partially precipitated with it. Removal of the albumoses by ammonium sulphate or by trichloroacetic acid does not interfere with the subsequent precipitation of the bases by ammoniacal silver solution; zinc sulphate, however, does; but even with the ammonium sulphate method, there is considerable loss of the bases. Besides albumoses, other substances, such as nucleic acid, interfere with the results; in fact, in extracts of organs much worse results are obtained than in artificial mixtures. The lead acetate method, also, is untrustworthy. Much the same is true for uric acid, and the best results were obtained by employing Stad-hagen's method of extracting the organs with 0.5 per cent. sulphuric acid. W. D. H.

Detection of Salicylic Acid in Presence of Citric Acid. By A. CONRADY and by OTTO LANGKOPF (*Chem. Centr.*, 1900, ii, 596; from *Apoth. Zeit.*, 15, 412, 462; *Pharm. Centr.*, 41, 411, 464).—Langkopf (this vol., ii, 695) has stated that citric acid prevents the reaction between ferric chloride and salicylic acid, and recommends a preliminary extraction of the latter with a mixture of ether and light petroleum. CONRADY considers that the failure to produce a violet colour is due to reduction of the ferric salt, since it can be developed by adding an oxidising agent (nitric acid or hydrogen peroxide).

LANGKOPF replies to Conrady that ferric chloride is not reduced by citric or tartaric acid, and denies that the violet colour is developed by adding nitric acid or hydrogen peroxide.

CONRADY, in rejoinder to Langkopf, states that he worked with a 1 per cent. solution of salicylic acid, Langkopf having employed one of only 0.1 per cent., and admits that below 1 per cent. the addition of an oxidising agent is ineffectual.

LANGKOPF states that the explanation of Conrady's results is, that on mixing ferric chloride with citric acid, ferric citrate is produced which has no action on salicylic acid. The addition of any strong acid prevents the formation of ferric citrate. Conrady's hydrogen peroxide probably contained free sulphuric acid. M. J. S.

Detection of Salicylic Acid in the Presence of Citric Acid. By J. E. GEROCK (*Chem. Centr.*, 1900, ii, 597; from *Pharm. Centr.*, 41, 464).—With reference to the controversy between Langkopf and Conrady, it is to be observed that all soluble acids are capable of preventing the ferric reaction of salicylic acid if present in sufficient excess. The violet coloured substance is to be regarded as salicylic acid in which the hydrogen of a hydroxyl group is replaced

by triatomic iron, and it is not formed if another acid, even citric, is present, for which iron has a greater affinity. M. J. S.

Detection of Salicylic Acid in Presence of Citric Acid. By A. KLETT (*Chem. Centr.*, 1900, ii, 545; from *Pharm. Centr.*, 41, 452).—Jorissen's method for detecting salicylic acid in beer serves equally well for lemon juice. Ten c.c. of the juice are mixed with 4 drops of a 10 per cent. solution of sodium nitrite, 4 drops of acetic acid, and 1 drop of a 10 per cent. copper sulphate solution, and heated to boiling. Salicylic acid produces a blood red coloration, which is best observed just as the liquid begins to boil. M. J. S.

Detection of Salicylic Acid in Milk. By P. SÜSS (*Chem. Centr.*, 1900, ii, 545; from *Pharm. Centr.*, 41, 437).—The presence of 0.2 per cent. of citric acid does not prevent the detection of 0.005 gram of salicylic acid in 100 c.c. of milk.

One hundred c.c. of milk are coagulated by warming at 80° with 1.5 c.c. of a 20 per cent. solution of calcium chloride, and the filtrate allowed to drop through 50 c.c. of ether, which is then evaporated in a porcelain basin and tested by running in from the edge 1—2 drops of dilute ferric chloride solution diluted with 10 c.c. of water.

M. J. S.

Estimation of Hippuric Acid. By FERDINAND BLUMENTHAL (*Chem. Centr.*, 1900, ii, 447; from *Zeit. klin. Med.*, 40, 3—4).—Three hundred c.c. of human urine are rendered alkaline with sodium carbonate and evaporated to dryness. The residue is extracted twice with 150 c.c. of 96 per cent. alcohol on a warm water-bath, and the alcoholic filtrate evaporated to a syrup. This is dissolved in 50 c.c. of water, acidified with 10 c.c. of 20—25 per cent. hydrochloric or sulphuric acid, and shaken with 200 c.c. of ether containing 20 c.c. of alcohol; the ethereal layer is then shaken with 75 c.c. of water and finally distilled. The extraction is repeated four times, and the ether residues are then dissolved in 20 c.c. of water and introduced into a Kjeldahl flask. (If much colouring matter is present, it is removed by shaking the solution in a separating funnel with 15 c.c. of chloroform.) The nitrogen is then estimated in the usual manner, and from its amount the hippuric acid is calculated.

The process is attended with a loss of about 15 per cent. of the hippuric acid present, but suffices for the comparative clinical examination of urine. L. DE K.

A Multiple Fat Extractor. By CHARLES L. PENNY (*Amer. Chem. J.*, 1900, 24, 242—249).—The apparatus is a modification of the Soxhlet extractor. Its essential part is a chamber made of a nearly horizontal brass cylinder 2 inches and a half in diameter and 30 inches long, wherein may be placed a semicircular rack holding 51 shallow capsules containing the samples to be extracted. The cylinder has a capacity of about 2400 c.c. The other parts of the apparatus are a vessel in which the extracting liquid is boiled by means of steam passing through lead coils, block tin condensers, and the usual syphon arrangement.

The milk is dried in the capsule with addition of coarse sand or

asbestos; after being weighed, the capsule is placed in the extractor, ether, or better, light petroleum boiling below 100° , being used as the extracting liquid. The capsule is then dried and reweighed, the loss representing the fat. Cream or butter must be absorbed in asbestos or glass wool.

L. DE K.

Variation in Milk Solids; Control of Milk Supply. By A. REINSCH and H. LÜHRIG (*Zeit. Nahr. Genussm.*, 1900, 3, 521—524).—The authors communicate fifty experiments from which it again appears that milk, even before it actually turns sour, may apparently have lost as much as 0.6 per cent. of solids owing to decomposition. This does not, however, affect the sp. gr. of the milk, so that as a rule more trustworthy results are obtained by calculating the total solids from the sp. gr. and the fat than by a direct estimation. From this it also follows that it is very risky to calculate the fat from the sp. gr. and the solids actually determined.

When dealing with sour milks not more than 3 days old, the sp. gr. of the serum should be taken as affording the only safe evidence as to the addition of water. It is also incidentally remarked that total solids cannot be accurately estimated in sour milk liquefied with ammonia.

L. DE K.

Estimation of Fat in Condensed Milk. By ALBERT E. LEACH (*J. Amer. Chem. Soc.*, 1900, 22, 589—591).—Forty grams of the well-mixed sample are diluted with water and made up to 100 c.c. and 25 c.c. of this solution introduced into an ordinary Babcock test-bottle. After nearly filling with water, 4 c.c. of a 7 per cent. solution of copper sulphate are added and the whole is whirled, preferably without heating, to make the precipitate settle. The supernatant liquid is then drawn off with a pipette, over the bottom of which a small wisp of absorbent cotton is first twisted to serve as a filter; this is afterwards wiped off into the bottle by rubbing against its inner side.

The precipitate which contains all the fat is washed twice to remove all cane sugar, water is then added to represent the usual volume of milk used in the experiment, and the usual Babcock sulphuric acid process applied. The result of the reading multiplied by 1.8 equals the percentage of fat.

L. DE K.

Estimation of Fat in Sweetened Condensed Milk. By JOSEPH F. GEISLER (*J. Amer. Chem. Soc.*, 1900, 22, 637—645).—Fat in condensed milk may be estimated with reasonable accuracy by the Adams' or coil process, provided not more than 1 gram of the sample is operated on, and that the extraction is continued for about 5 hours.

Light petroleum of low boiling point, or a mixture of 15 per cent of this with dry ether, is recommended as the extracting liquid.

L. DE K.

Estimation of Fat in Sweetened Condensed Milk by the Babcock Test. By E. H. FARRINGTON (*Amer. Chem. J.*, 1900, 24, 267—270).—When estimating fat in condensed milk by the centrifugal methods, it is advisable to first remove the added sugar as this

causes a very unsatisfactory reading of the fatty layer (compare preceding abstracts). 40—60 grams of the sample are weighed into a 200 c.c. flask, about 100 c.c. of water are added to dissolve the milk, and after diluting to the mark and shaking, 17.6 c.c. are measured into a Babcock test-bottle. Three c.c. of sulphuric acid are added and the bottle is whirled for 6 minutes in a steam-heated turbine centrifuge at a speed of 1000 revolutions.

The whey is now poured off, 10 c.c. of water and 3 c.c. of acid are added, the curd is well shaken and the bottle whirled a second time; this treatment practically removes all the sugar and after pouring off the washings, the residual curd and fat are treated with 10 c.c. of water and 17.5 c.c. of sulphuric acid and the operation conducted as in the case of an ordinary milk.

L. DE K.

Estimation of the Volatile Acids in Butter by Leffmann-Beam's Glycerol-Soda Process. By ANTON SEYDA (*Chem. Zeit.*, 1900, 24, 752—753).—The amount of sulphuric acid stated to be sufficient to decompose the soap when butter is saponified with Leffmann-Beam's solution of sodium hydroxide in glycerol has been found by the author to be often insufficient. The amount should be doubled and a correspondingly smaller quantity of water used to dissolve the soap. In the case of doubtful results, it is advisable to check the work by the ordinary Reichert-Meissl process.

L. DE K.

Chemical Action of Mould on Butter. By JOS. HANUŠ and ALB. STOCKY (*Zeit. Nahr. Genussm.*, 1900, 3, 606—614).—A series of experiments with nine different kinds of fungus on butter for various lengths of time.

In the first experiment the butter was inoculated with the fungi and exposed in thin layers to moist air in the dark. After three months the various portions and also the non-inoculated original were analysed in the usual way. From the figures recorded it appears that the effect of the different fungi is practically the same; the only figure seriously affected is the acidity number, which was raised some 24 degrees.

In another experiment which lasted one year, the sample was inoculated with *Mucor mucedo* and the only figures notably affected were the saponification and ether numbers and the molecular weight of the free volatile acids. Further experiments have shown that the fungi at first thrive on the casein and lactose and then live at the expense of the glycerol; they also cause the oxidation of the lower volatile acids contained in the liberated fatty acids.

L. DE K.

The Halphen Colour Test and its Value for the Detection of Cotton Seed Oil. By ROZIER D. OILAR (*Amer. Chem. J.*, 1900, 24, 355—373).—To dispense with the use of amyl alcohol and a bath of boiling aqueous sodium chloride in the Halphen test (*Abstr.*, 1898, ii, 358) is a disadvantage rather than an advantage as claimed by Soltsien (*Abstr.*, 1899, ii, 323); ethyl alcohol gives a less pronounced coloration than amyl alcohol. The examination of a large number of the common oils and fats shows that the test is given by cotton seed oil alone, and the value of the reaction is enhanced by the fact that none

of the ordinary colouring matters or adulterants responds to it. The test is capable of indicating rather less than 0.1 per cent. of cotton-seed oil in fresh, colourless lards, and is very pronounced with 1 per cent. of the oil. The test can be used more or less quantitatively by comparing the depths of colour produced with those obtained with equally concentrated volumes of known mixtures of lard and cotton seed oil; the results are most satisfactory with lards containing less than 1 per cent. of the oil (compare Strzyzowski, this vol., ii, 325).

W. A. D.

Maripa Fat. By W. P. H. VAN DEN DRIESSEN MAREEUW (*Chem. Centr.*, 1900, ii, 637—638; from *Ned. Tijds. Pharm.*, 12, 245—249).—Maripa fat, obtained by boiling or pressing the fruit of *Palma maripa*, is colourless or faintly yellow, has a slight taste and pleasant odour, and is used in the West Indies instead of butter. It has a sp. gr. 0.8686 at 100°, melts at 26.5—27°, solidifies at 24—25°, and has an acid number 31.095, saponification number 270.5, ether number 239.40, Hehner number 88.88, Reichert-Meissl number 4.45, and Hübl's iodine number 17.35. The fatty acids melt at 27.5—28.5°, solidify at 25°, and have a sp. gr. 0.823, and Hübl's iodine number 12.15.

E. W. W.

Simple Analysis of Wool Fat. By HUGO BORNTÄGER (*Zeit. anal. Chem.*, 1900, 39, 505).—Wool fat consists mainly of oleic, stearic, margaric, and palmitic acids, with small amounts of water and insoluble impurities. A gram of the fat is dried at 110° to estimate water, then dissolved in 50 c.c. of hot absolute alcohol, and the insoluble matter collected on a weighed filter. The alcoholic filtrate and washings are concentrated to 50 c.c. and left at rest for 24 hours in the cold. The solid fatty acids crystallise out and are weighed, after washing three times with cold alcohol and drying at 105°. The remainder is regarded as oleic acid.

M. J. S.

Estimation of Aldehydes by Means of Hydrazines. I. Estimation of Vanillin. By JOS. HANUŠ (*Zeit. Nahr. Genussm.*, 1900, 3, 531—537).—The aqueous solution of vanillin is mixed with a hot solution of *p*-bromophenylhydrazine in such proportion that 2—3 parts of the hydrazine will be present for 1 part of vanillin. After 4—5 hours, the crystalline precipitate is collected in a weighed Gooch crucible containing asbestos, washed with hot water, dried at 100° and weighed. One part of vanillin yields 2.105 parts of the hydrazine compound.

Experiments with other aldehydes are in progress. L. DE K.

Detection of Aldehyde in Vinegar prepared by Fermentation. By CARL BÖTTINGER (*Chem. Zeit.*, 1900, 24, 793—794).—Vinegars prepared by fermenting alcoholic liquors always contain traces of aldehyde, whereas diluted acetic acid made to resemble vinegar is devoid of that substance.

The aldehyde may be tested for in the usual manner by pouring some of the vinegar on to a solution of a few milligrams of resorcinol in 4 c.c. of sulphuric acid contained in a test-tube, and noticing the characteristic ring at the place of contact. It is remarkable that

when dealing with a true fermentation vinegar, the reaction may also be obtained, although in a lesser degree, with the residue left on evaporation; this, of course, cannot contain any free aldehyde, but may contain a non-volatile compound of it. L. DE K.

New Colour Reaction for Citral and certain other Aromatic Compounds. By HERBERT E. BURGESS (*Analyst*, 1900, 25, 265—266).—Ten grams of mercuric sulphate are dissolved in, and made up to 100 c.c. with, 25 per cent sulphuric acid. Two c.c. of the substance to be tested are put into a small phial fitted with a cork, 5 c.c. of the reagent are added, the whole is vigorously shaken and the colour noticed at once, and also after 10 minutes. The following reactions are characteristic: Cinnamaldehyde, formaldehyde, acetaldehyde, benzaldehyde, and anisaldehyde give no reaction. Citral gives a transient, bright red coloration, and a whitish compound floating on the surface; citronellal a fairly permanent yellow coloration; limonene faint flesh coloration which instantly disappears; linalyl acetate a permanent brilliant violet coloration; linalool a deep violet coloration; caryophyllin a yellowish coloration; eugenol a slight violet coloration after a time, and terpineol a flesh coloration and precipitate.

Oil of cassia gives a yellowish compound floating on the surface and no reduction on shaking. Oil of cinnamon forms a brown compound and a slight violet-coloured aqueous layer; after a time the whole becomes a solid black mass. Oil of cloves gives a violet aqueous layer which becomes darker when kept. L. DE K.

Chemicotoxicology of Sulphonal and Analogous Compounds. By DIOSCORIDE VITALI (*Chem. Centr.*, 1900, ii, 646—647; from *Boll. Chim. Farm.*, 39, 461, 497).—To isolate sulphonal from an organic liquid, the liquid is evaporated to dryness, extracted with hot 90 per cent. alcohol, the alcoholic extract filtered after cooling, and distilled. The residual aqueous liquid is filtered while hot, made feebly alkaline with potassium hydroxide, and shaken with ether. The ethereal solution when evaporated leaves a colourless residue of sulphonal, easily recognised under the microscope by the characteristic dendritic form of its crystals. The reactions proposed by Schwartz, Vulpius and others depending on fusion with alkali are not characteristic as they are produced by other sulphur compounds.

Sulphonal may, however, be detected by the following reactions. The substance is heated with three parts of powdered potassium hydroxide, when the liquid becomes yellow, then red, and the colour changes to blue on adding water. On acidifying with hydrochloric acid, an ephemeral violet colour is produced and sulphur separates, whilst sulphur dioxide is evolved, and a sulphate can be detected in the solution. The thiosulphate formed can also be recognised by adding potassium nitrite and an acid, when a transient, yellow colour is produced by the solution of nitric oxide in thiosulphuric acid. That a polysulphide is also formed can be shown by adding sodium nitroprusside.

The homologues of sulphonal (trional and tetronal—see Abstr., 1889, 1233) can be distinguished from sulphonal by their crystalline form and lower melting points. Sulphonal is not altered by the pre-

sence of putrefying matter. All three sulphones pass, to some extent, unchanged into the urine.
M. J. S.

Analysis of Gutta Percha. By HUGO BORNTRÄGER (*Zeit. anal. Chem.*, 1900, 39, 502—504).—Of the three substances, gutta, fluavil, and alban, of which gutta percha is composed, the last is not a chemical individual, but consists approximately of 30 per cent. of a pale resin oil boiling at 200°, 30 per cent. of a dark yellow oil boiling at 250° and 40 per cent. of a solid resin resembling colophony. For the analysis of the crude material, moisture is estimated by drying in an air current at 100°, and woody fibre and earth by dissolving 1 gram in hot benzene. The benzene solution is then concentrated to 50 c.c., mixed with 100 c.c. of absolute alcohol, and kept at 100° for 2 hours. The gutta precipitates, and is weighed after washing with hot alcohol. The alcoholic solution is concentrated to 50 c.c. and cooled in a weighed basin. The fluavil separates and is weighed after washing with cold alcohol and drying at 80°, but as it is more volatile than alban it is better to estimate it from the difference after evaporating the solution containing the alban and drying the latter at 80°
M. J. S.

Estimation of Glycyrrhizin in Liquorice Extract. By B. HAFNER (*Chem. Centr.*, 1900, ii, 501; from *Zeit. Oesterr. Apoth. Verein*, 38, 241—244. Compare this vol., ii, 328).—The author has shown that the well-known insolubility of glycyrrhizin in dilute sulphuric acid is not due to a chemical combination. Pure glycyrrhizin can only be obtained by extraction with alcoholic sulphuric acid, coupled with purification by acetone as described in the first paper. More glycyrrhizin may apparently be extracted by means of ammoniacal water, but in that way an impure product is obtained. All samples do not yield an equally pure product.
L. DE K.

Analysis of Cayenne Pepper. By GEORG GREGOR (*Zeit. Nahr. Genussm.*, 1900, 3, 460—471).—The author has proved that the plant (*Capsicum annuum*) does not assimilate barium or lead salts when either of these has been purposely added to the soil. Should salts of these metals be found in the commercial article, it may be safely assumed that they have been wilfully added.

It is also stated that the only way of ascertaining the genuineness of cayenne pepper (the ground fruit) is by a thorough microscopic examination. A somewhat high ash does not necessarily point to adulteration; should it, however, amount to 10 per cent., it is as well to treat it with hydrochloric acid and test both the soluble and insoluble portions.
L. DE K.

Estimation of Santonin. By KARL THAETER (*Arch. Pharm.*, 1900, 238, 383—387. Compare *Abstr.*, 1898, ii, 59; 1899, ii, 619; this vol., ii, 122, 583).—The loss in the author's process is not more than about 10 per cent. As a further improvement in the method the recommendation is made that, after the boiling with milk of lime, the alkaline liquid should be slightly acidified with sulphuric acid, and warmed until crystals of santonin begin to separate, before the solution of aluminium acetate is added.
C. F. B.

Detection of Coal-Tar Dyes in Fruit Products. By A. L. WINTON (*J. Amer. Chem. Soc.*, 1900, 22, 582—588).—The author communicates his experiences with some of the recognised methods for the detection of coal-tar colours in foods.

Arata's "wool process" is satisfactory; it is, however, preferable to apply the confirmatory tests to the wool itself and not to the colouring matter obtained from it, because some coal-tar dyes are not properly extracted by amyl alcohol from an alkaline solution. It is also pointed out that some natural colouring matters such as chlorophyll merely form a coating on the wool which may be easily rubbed off, whilst coal-tar colours act as true dyes.

Girard and Dupre's processes (removal of the dye with amyl alcohol either from an alkaline or acid solution and treating the alcoholic extract with wool) give good results. Girard's process for acid magenta (treatment with potassium hydroxide and mercuric acetate and then acidifying the filtrate with sulphuric acid) is useful in the examination of fruit juices and syrups but unsatisfactory in the case of jellies. Cazeneuve's mercuric oxide method, although to be recommended for wines, is not satisfactory for the examination of jellies but may, perhaps, answer for fruit juices and syrups. L. DE K.

Detection of Indican in Pathological Urine. By A. KLETT (*Chem. Zeit.*, 1900, 24, 690).—Ammonium persulphate is much better than bleaching powder as a reagent for indican in urine. A crystal of ammonium persulphate is added to a mixture of urine (10 c.c.) and 25 per cent. hydrochloric acid (5 c.c.), and the mixture shaken with chloroform; the imparting of a blue colour to the latter proves the presence of indican. J. J. S.

Ehrlich's Diazo-reaction. By G. WESENBERG (*Chem. Centr.*, 1900, ii, 67—68; from *Apoth. Zeit.*, 15, 326—328).—The reagent is generally prepared as follows. One gram of sulphanic acid is dissolved in water containing 50 c.c. of hydrochloric acid and diluted to a litre. When required, 10 c.c. of the solution are mixed with 2 c.c. of a 0.5 per cent. solution of sodium nitrite, and 10 c.c. of the mixture followed by 2.5 c.c. of ammonia are then added to 10 c.c. of the urine to be tested, and the whole is vigorously shaken. If a reaction is obtained and the red liquid exposed to the air for 24 hours, a greenish deposit is obtained, but it often fails to form in cases of tuberculosis.

The author advises that no alterations should be made in the application of the test. It is stated that the diazo-reaction may be caused when naphthalene has been administered; bilirubin also gives the test, and should be removed by a preliminary treatment with lead acetate or animal charcoal. On the other hand, preparations of tannic acid seem to prevent the reaction. L. DE K.

Ehrlich's Diazo-reaction for the Recognition of some recently introduced Morphine Derivatives. By LUIGI CARCANO (*Chem. Centr.*, 1900, ii, 288; from *Boll. Chim. Farm.*, 39, 425—428).—Ehrlich's reagent in the presence of ammonia (see preceding abstract) acts on heroine (diacetylmorphine), forming a red, crystalline azo-compound of the formula $\text{NH}_4 \cdot \text{SO}_3 \cdot \text{C}_6\text{H}_4 \cdot \text{N}_2 \cdot \text{C}_{21}\text{H}_{22}\text{O}_5\text{N}$. Morphine

gives a similar wine-red but less intense coloration. The reagent is particularly useful for the detection of small quantities of dionine (morphine ethyl ether) in codeine (morphine methyl ether). 0.01 gram of the suspected substance is dissolved in 1 c.c. of water, a few drops of ammonia are added, and then Ehrlich's reagent drop by drop. Pure codeine gives a fine yellow, but dionine a red colour. Narcotine, narceine, papaverine, and thebaine give either a faint yellow colour or no reaction at all.

L. DE K.

Assay of Opium. By J. B. NAGELVOORT (*Pharm. Weekblad*, 1900, No. 24, 1—8).—The acidimetric process introduced by Prescott and Gordin (Abstr., 1899, ii, 714) is recommended. No morphine is removed from the sodium chloride mixture by treatment with benzene, which merely dissolves the inferior opium alkaloids. The results are generally higher than those obtained by the gravimetric process of the U.S.P., but the difference is not always as high as 3 per cent.

A drawback to the method is the long time it takes, also the great waste of alcohol and chloroform, but these might be recovered by distillation.

L. DE K.

Modified Alkalimetric Method for the Valuation of Opium, and other Pharmaceutical Drugs and Preparations that contain Alkaloids. By HARRY M. GORDIN (*Arch. Pharm.*, 1900, 238, 335—341).—The method already described (compare Abstr., 1899, ii, 714, but especially this vol., ii, 110) has been modified slightly. *N*/40 sulphuric acid and *N*/40 potassium hydroxide are used, in place of *N*/20 solutions, in the titration of the alkaloid, which may be extracted in any suitable manner. If it has to be extracted from a solution alkaline with potassium hydroxide, say by shaking with a mixture of ether and chloroform, the extract will contain a little alkali, and must be freed from this before it is evaporated, best by shaking with a little ignited magnesia and filtering. In the case of alkaloids which dissolve with difficulty in very dilute acids, such as strychnine and hydrastine, it is better not to evaporate the ethereal solution, but to shake it with the excess of acid, and then distil off the ether cautiously before titrating.

The method was applied to opium (1 c.c. *N*/40 acid per gram of the sample = 0.71 per cent. of morphine), *nux vomica* (1 c.c. *N*/40 acid = 0.0091 gram alkaloid, reckoned as equal parts of strychnine and brucine), and cinchona bark (1 c.c. *N*/40 acid = 0.0077 gram alkaloid reckoned as equal parts of quinine and cinchonidine), and also to the commercial extracts of the last two substances and of *Hydrastis canadensis*.

C. F. B.

Action of Iodine on Aconitine and Caffeine. By CARL KIPPENBERGER (*Zeit. anal. Chem.*, 1900, 39, 435—450).—The author has endeavoured to extend to aconitine and caffeine the methods of titration based on the formation of alkaloid periodides (Abstr., 1886, 282, 682; 1899, ii, 534, 584). With caffeine, the presence of a considerable amount of free mineral acid is essential to the precipitation of the periodide; a portion of the caffeine always escapes precipitation, but this may be reduced to inconsiderable traces by using a large excess

of the iodine solution. The amount of iodine consumed varies with the conditions of the titration; it generally approximates to 4 atoms for one molecule of caffeine, except in the case where the alkaloid hydrochloride is converted into hydriodide by a solution of silver iodide in potassium iodide (Abstr., 1896, ii, 682), when it is very close to 2 atoms. The iodine solution must therefore be standardised against weighed caffeine under conditions identical with those of the titration. Aconitine can be better estimated by alkalimetric titration (this vol., ii, 637) than by means of iodine. M. J. S.

Estimation of Nicotine, Amount of Nicotine in New South Wales Tobaccos. By G. HARKER (*Chem. News*, 1900, 81, 273).—Kissling's and Biel's methods give similar results; but the modification of the latter involving the weighing of the double sulphates of nicotine and ammonia, and also attempts to estimate nicotine volumetrically in presence of ammonia, have not proved successful. No loss of nicotine has been observed during the evaporation of its ethereal solution. Four varieties of New South Wales tobaccos gave the following percentages of nicotine:—Manilla, 1.95; Tamworth, 2.36; Tumut, 3.84; Bathurst, 4.53. D. A. L.

Estimation of Strychnine. By E. H. FARR and ROBERT WRIGHT (*Pharm. J.*, 1900, [iv], 11, 82—85).—In view of Schweissinger's criticisms (*Pharm. J.*, 1885, [iii], 16, 447), the authors have examined the pharmacopœial process for the assay of nux vomica preparations (compare Dunstan and Short, Abstr., 1883, 689, 1175). Strychnine ferrocyanide is not quite insoluble in water acidified with sulphuric acid, and if precipitated in presence of brucine, the latter can never be entirely separated. If the amount of brucine is large, this alkaloid may form more than half the precipitate; almost the whole, however, can be removed by washing with acidified water. The authors recommend that not more than 5 c.c. of the liquid extract or 30 c.c. of the tincture should be assayed, and that 200 c.c. of wash water at a stated temperature (38°) should be employed, a correction being made for the strychnine dissolved by it. R. L. J.

Behaviour of Proteids to Alkaloid Reagents, and a Method of Estimating Combined Hydrochloric Acid. By OTTO COHNHEIM and H. KRIEGER (*Zeit. Biol.*, 1900, 40, 95—116).—The combinations of albumoses and hydrochloric acid which are formed in the stomach are salts which react acid to litmus, phenolphthalein, and other indicators, and neutral to Congo-red, methyl-violet, &c. If a mixture contains only hydrochloric acid and such acid proteoses, the use of such indicators enables the free acid to be estimated; but this is not the case with the contents of the stomach, where salts and other acids are also present. For the estimation of acid-proteoses, salting-out is a method which was found impracticable, but certain alkaloid reagents precipitate them readily. Sodium phosphotungstate, for instance, will not precipitate proteid, but it will precipitate proteid which is combined with hydrochloric acid. In this, proteids resemble Hantzsch's pseudo-ammonium bases. Various alkaloid reagents were tested with artificial mixtures and stomach contents. The results

with calcium phosphotungstate and potassio-mercuric iodide were satisfactory, and agree well with those obtained by Sjöqvist's more complicated method. W. D. H.

Modification of Ritthausen's Method of Determining Proteids. By F. BARNSTEIN (*Landw. Versuchs.-Stat.* 1900, 54, 327—336).—Instead of gradually adding sodium hydroxide until the solution is neutral, it is proposed to add a definite volume of aqueous sodium hydroxide, insufficient to completely precipitate the copper. In this manner, the difficulty of exactly neutralising coloured liquids is avoided, and there is a further advantage that the precipitate settles quickly, whilst the liquid filters more easily than is the case with Stutzer's method. The process is as follows.

The substance is boiled with 50 c.c. of water, or, if starchy, is heated for 10 minutes in a water-bath, treated with 25 c.c. of a solution of copper sulphate (containing 60 grams of the crystallised salt per litre); 25 c.c. of aqueous sodium hydroxide (12.5 : 1000) is then added, the liquid being stirred; the supernatant liquid is poured through a filter, the precipitate washed several times by decantation, and finally on the filter. Washing is continued until the solution no longer shows a reaction with potassium ferrocyanide or barium chloride. The nitrogen is then determined by the Kjeldahl process without removing the precipitate from the filter.

A number of results are given agreeing very nearly with those obtained by Stutzer's method. In the case of tea, sugar-beet, lupins, and tobacco, however, somewhat high results are obtained (+0.07 to 0.19 per cent). The results of special determinations showed that asparagine, guanine, and betaine are not precipitated by copper hydroxide. Probably the malt-germ extract with which the substances were mixed kept the guanine in solution (compare Bosshard and Schulze, *Landw. Versuchs.-Stat.*, 1887, 33, 132). Tobacco which had been boiled with 40 per cent. alcohol, acidified with acetic acid (Kellner, *Landw. Versuchs.-Stat.*, 24, 439) still gave a rather higher result (+0.09 per cent). than by Stutzer's method. The new modification is, however, suitable for most purposes.

As regards peptones, it was found that both with vegetable and animal albumin the precipitation was not complete, but in the modification adopted by the author the copper precipitate contained more nitrogen than was obtained by Stutzer's method. N. H. J. M.

Precipitation of Proteids. By HENRIK SCHJERNING (*Zeit. anal. Chem.*, 1900, 39, 545—566).—In continuation of earlier work on this subject (Abstr., 1896, ii, 631; 1898, ii, 271, 416, 658), the author inquires how far his proposed reagents, and those suggested by others, fulfil the three conditions (I) of giving clear filtrates and washings, (II) of invariably precipitating certain groups of proteids, (III) of precipitating no other nitrogenous organic substances. The reagents investigated (in addition to his own) are (1) Bromine water (Abstr., 1898, ii, 320), (2) tannic acid, (3) Stutzer's copper reagent prepared by Fassbender's method (Abstr., 1881, 205), (4) phosphotungstic acid. Experiments with about 20 different nitrogenous substances show that none of the proposed reagents conforms completely with condition

III, but that the author's six reagents are by far the safest inasmuch as, with the exception of magnesium sulphate, they precipitate very few of these substances, and then in most cases in but small amount. On the other hand, many of these nitrogenous substances are precipitated, and sometimes in large amounts, by bromine water, Stutzer's reagent, and especially by phosphotungstic acid, whilst in other cases precipitates are produced which pass through filter-paper, but would be retained if formed simultaneously with proteid precipitates. Uranium acetate in presence of phosphates and mercuric chloride precipitates ammonia from the acetate. The errors so produced can be avoided by precipitating the phosphoric acid by lead acetate (not in excess) at 50° before adding uranium acetate, or by heating the precipitate with magnesia; the precipitation of ammonia from its acetate by mercuric chloride is prevented by the presence of alkali chlorides, especially ammonium chloride, or the use of mercuric chloride can be avoided altogether by employing lead acetate, which throws down the same proteids. As regards the actual precipitation of proteids by the reagents mentioned, it is shown that bromine water causes very incomplete precipitation and is very liable to give turbid filtrates, that tannic acid and Stutzer's reagent precipitate albumoses and peptones incompletely or not at all, and that phosphotungstic acid in some cases fails to conform with condition II. Laszczyński's proposal to coagulate the proteids by heating at a pressure of $1\frac{1}{2}$ atmospheres is likewise shown to give very imperfect results. In cases where large amounts of salts of the light metals are present all the reagents fail to give quantitative results, with the exception of magnesium sulphate, stannous chloride, and probably Stutzer's reagent and tannic acid.

M. J. S.

ERRATA.

VOL. LXXVI. (ABSTR., 1899).

PART I.

Page Line
960 19* for " $C_{15}H_{20}ON_2Br_2, H_2PtCl_6$ " read " $(C_{15}H_{20}ON_2Br_2)_2, H_2PtCl_6$."

VOL. LXXVIII. (ABSTR., 1900).

PART I.

24 16 for "8-nitro-1-nitroso-1-naphthol" read "5-nitro-4-nitroso-1-naphthol."
 ,, 20 ,, "1:3:5:4 or 1:3:8:4" read "2:4:8:1 or 2:4:5:1."
 ,, 15* ,, "1:3:5:4" read "2:4:8:1."
 184 10* ,, "oil of cumin" read "oil of caraway."
 255 14 ,, "2-Nitro-" read "10-Nitro-"
 ,, 14, 15 ,, "2-Amino-" read "10-Amino-"
 ,, 16 ,, "2-nitrophenyl" &c., read "10-nitro-7-phenyl" &c.
 ,, 25 ,, "2-amino-3-dimethylamino-5-"
 ,, read "10-amino-9-dimethylamino-7-"
 ,, 14* ,, "2-amino-3-anilinophenylnaphthaphenazonium-5-"
 ,, read "10-amino-9-anilino-7-phenylnaphthaphenazonium"
 ,, 6* ,, "2-amino-5-phenyl" &c., read "10-amino-7-phenyl" &c.
 443 8*, 4*, 3* }
 444 3, 2* } for "lactone" read "anhydride."
 535 15 for "or Trimethylene" read "on Trimethylene."
 578 17* ,, "TCHERDINTZEFF" read "TSCHERDINTZEFF."
 686 13* ,, "bromoacetone" read "bromoacetophenone."

PART II.

23 14 for "20" read "1899."
 139 6 ,, "+ 3HO" read "+ 3H₂O."
 461 18 ,, "Methyl Acetate" read "Ethyl Ether."
 ,, 28 ,, "ethyl acetate" read "ethyl ether."
 474 13 ,, "60°" read "- 60°."
 540 11*, 9* ,, "Hg₆K" read "Hg₆Na."
 ,, 10* ,, "Hg₅K" read "Hg₅Na."
 551 9* ,, "Er₂O" read "Er₂O₃."
 567 24* }
 568 2 } "BARTLET" read "BARTLETT."
 600 24 ,, "D'ACHIARDI" read "D'ACHIARDI."
 657 top ,, "KUZNETZOFF" read "KUTZNETZOFF."
 702 18* ,, "laranskite" read "loranskite."

* From bottom.